INTRODUCTION TO GROUND-STATE DENSITY FUNCTIONAL THEORY (GS-DFT)

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MANTRA OF CORRELATED-WAVEFUNCTION THEORY:
THE RIGHT ANSWER FOR THE RIGHT REASON (BUT AT A HIGH PRICE, AND ONLY FOR FEW-ELECTRON SYSTEMS.)

MANTRA OF DENSITY FUNCTIONAL THEORY:
ALMOST THE RIGHT ANSWER FOR ALMOST THE RIGHT REASON AT ALMOST THE RIGHT PRICE FOR ALMOST ALL SYSTEMS OF INTEREST.

THE HISTORY OF DFT SHOWS THE POWER OF AN EXISTENCE THEOREM.
OUTLINE

CONNECTION BETWEEN GROUND-STATE DFT AND TIME-DEPENDENT DFT

MOTIVATION FOR GS-DFT

BRIEF HISTORY AND CURRENT STATE OF GS-DFT

TIME FOR YOUR QUESTIONS AND COMMENTS

SOME FUNDAMENTAL THEOREMS AND PROOFS OF GS-DFT (HANDWRITTEN APS TUTORIAL)

TIME FOR YOUR QUESTIONS AND COMMENTS
CONNECTION BETWEEN GROUND-STATE DFT AND TIME-DEPENDENT DFT

TD-DFT DESCRIBES HOW THE DENSITY OF A MANY-ELECTRON SYSTEM, SUBJECT TO A POSSIBLY TIME-DEPENDENT SCALAR MULTIPLICATIVE EXTERNAL POTENTIAL, EVOLVES IN TIME FROM AN INITIAL WAVEFUNCTION (AND THEREFORE THE POSSIBLE EXCITATION ENERGIES OF THE SYSTEM). GS-DFT IS THE STATIC OR SLOWLY-VARYING-IN-TIME LIMIT OF TD-DFT WHEN THE INITIAL STATE IS THE GROUND-STATE, AND PROVIDES OR GUIDES THE APPROXIMATIONS OF TD-DFT. (BUT TD-DFT IS MUCH HARDER TO DEVELOP THAN GS-DFT.)
MOTIVATION FOR GROUND-STATE DFT

Materials include not only free atoms and atomic ions but also collections of atoms bonded together: molecules, nanostuctures, liquids, gels, and solids.

A material can be defined by its composition (how many atoms of each kind) and structure (where the atoms are relative to one another). Structure is determined by covalent, ionic, metallic, hydrogen, or van der waals bonds between the atoms.
MATERIALS DISPLAY MANY SURPRISING OR EMERGENT PROPERTIES, AND ALSO MANY USEFUL ONES. LIFE AND SUPER-CONDUCTIVITY ARE TWO EXAMPLES.

CHEMISTS AND CONDENSED MATTER PHYSICISTS WANT TO UNDERSTAND MATERIALS. MATERIALS SCIENTISTS WANT TO DESIGN USEFUL NEW MATERIALS.

EXPERIMENT KEEPS US GROUNDED IN REALITY, BUT IT IS TOO SLOW AND EXPENSIVE TO EXPLORE THE IMMENSE SPACE OF POSSIBLE MATERIALS.
MODELS WITH PARAMETERS FITTED TO EXPERIMENT CAN HELP US UNDERSTAND MATERIAL PROPERTIES, BUT THEY CANNOT PREDICT WHAT MATERIALS CAN EXIST AND WITH WHAT PROPERTIES.

THE ONLY PREDICTIVE AND MATERIALS-SPECIFIC THEORY IS THE QUANTUM MECHANICS OF MANY INTERACTING ELECTRONS. BUT STANDARD QUANTUM MECHANICS IS ALSO TOO SLOW FOR ALL BUT THE SMALLEST SYSTEMS.
THE MOST WIDELY-USED THEORY OF MATERIALS, AND THUS THE MOST-CITED AREA OF PHYSICS OR CHEMISTRY, IS DENSITY FUNCTIONAL THEORY (DFT), WHICH STARTS FROM STANDARD QUANTUM MECHANICS, THEN SHOWS THAT IN PRINCIPLE THE EXACT GROUND-STATE ENERGY AND ELECTRON DENSITY CAN BE PREDICTED FROM A FUNCTIONAL OF ELECTRON DENSITY. DFT FINDS COMPUTATIONALLY EFFICIENT APPROXIMATIONS TO THAT FUNCTIONAL, WITH A USEFUL ACCURACY THAT IMPROVES OVER TIME. DFT INTRODUCES AN AUXILIARY SYSTEM OF NON-INTERACTING ELECTRONS THAT OBEY SELF-CONSISTENT ONE-ELECTRON SCHROEDINGER EQUATIONS.
AT ORDINARY TEMPERATURES, THE ELECTRONS OF A MATERIAL ARE OFTEN IN OR CLOSE TO THEIR GROUND STATE, EVEN WHEN THE MORE MASSIVE NUCLEI OR NOT. FOR EXAMPLE, LIQUIDS ARE OFTEN COMPUTED BY AB INITIO MOLECULAR DYNAMICS, WHICH DESCRIBES THE CLASSICAL MOTION OF THE NUCLEI BUT COMPUTES THE FORCES ON THE NUCLEI AS GRADIENTS OF THE GROUND-STATE TOTAL ENERGY OF THE ELECTRONS, FROM GS-DFT.
BRIEF AND PARTIAL HISTORY OF GS-DFT

1926 SCHROEDINGER EQUATION FOR THE WAVEFUNCTION

1927 THOMAS-FERMI APPROXIMATION FOR THE GS DENSITY AND ENERGY, WITHOUT A WAVEFUNCTION

1928 HARTREE APPROXIMATION FOR SELFCONSISTENT ONE-ELECTRON WAVEFUNCTIONS

1930 HARTREE-FOCK MEAN-FIELD APPROXIMATION

1930 DIRAC LOCAL DENSITY APPROXIMATION FOR THE EXCHANGE ENERGY
1951 SLATER’s X-ALPHA METHOD AS A DENSITY FUNCTIONAL APPROXIMATION TO HARTREE-FOCK

1964 HOHENBERG-KOHN THEOREM: AN EXACT-IN-PRINCIPLE GS-DFT

1965 KOHN-SHAM THEOREM: EXACT-IN-PRINCIPLE ONE-ELECTRON EQUATIONS. THE LOCAL DENSITY APPROXIMATION FOR THE EXCHANGE-CORRELATION ENERGY, AN INTEGRAL OVER 3D SPACE OF A FUNCTION OF THE LOCAL ELECTRON DENSITY, CONSTRUCTED TO BE EXACT FOR A DENSITY THAT IS UNIFORM OR SLOWLY-VARYING-IN-SPACE.

1965-1972: LITTLE INTEREST, AND LITTLE EXPECTATION (EVEN FROM KOHN) THAT THE LOCAL DENSITY APPROXIMATION COULD BE USEFULLY ACCURATE. PHYSICISTS PREFERRED THE HARTREE APPROACH, AND CHEMISTS THE HARTREE-FOCK APPROACH.
1972 VON BARTH-HEDIN SPIN-DENSITY FUNCTIONAL THEORY

~1972 CONDENSED MATTER PHYSICISTS DISCOVER THAT MAKING A LOCAL SPIN DENSITY APPROXIMATION (LSDA) TO THE EXCHANGE-CORRELATION ENERGY IS VASTLY MORE ACCURATE THAN IGNORING THIS ENERGY (AS IN THE HARTREE APPROX.). THE XC ENERGY IS “NATURE”’S GLUE”, BONDING ONE ATOM TO ANOTHER.

1975-1976 LANGRETH AND PERDEW, ALSO GUNNARSSON AND LUNDQVIST, DERIVE THE EXACT ADIABATIC CONNECTION EXPRESSION FOR EXCHANGE-CORRELATION ENERGY, EXPLAINING WHY LSDA WORKS.
1979 LEVY DERIVES THE EXACT CONSTRAINED-SEARCH EXPRESSION FOR THE EXCHANGE-CORRELATION ENERGY

1981 PERDEW AND ZUNGER DESIGN A SELF-INTERACTION CORRECTION TO DENSITY FUNCTIONAL APPROXIMATIONS

1982 PERDEW, PARR, LEVY, AND BALDUZ DERIVE DFT FOR OPEN SYSTEMS WITH NON-INTEGRAL AVERAGE ELECTRON NUMBER

1984 RUNGE AND GROSS DERIVE TIME-DEPENDENT DFT
1980’s LEVY, LIEB, AND OTHERS DERIVE MANY EXACT MATHEMATICAL PROPERTIES OF THE EXACT DENSITY FUNCTIONALS FOR THE EXCHANGE AND CORRELATION ENERGIES

1980’s AND 1990’s LANGRETH AND MEHL, PERDEW AND WANG, BECKE, YANG, PARR, BURKE, AND ERNZERHOF DEVELOP GENERALIZED GRADIENT APPROXIMATIONS (GGA’s) TO THE XC ENERGY, AN INTEGRAL OVER 3D SPACE OF A FUNCTION OF THE LOCAL ELECTRON DENSITY AND ITS GRADIENT.

1993 BECKE PROPOSES HYBRID FUNCTIONALS THAT MIX A FRACTION OF EXACT EXCHANGE WITH GGA’s

1990’s DFT, ENDORSED BY JOHN POPLE, BECOMES POPULAR IN CHEMISTRY
1998 KOHN AND POPEL SHARE THE NOBEL PRIZE IN CHEMISTRY FOR DFT

2000’s DFT BECOMES POPULAR IN MATERIALS SCIENCE

2008 YANG, MORI-SANCHEZ, AND COHEN DERIVE DFT FOR FRACTIONAL SPIN

2015 SUN, RUZSINSZKY, AND PERDEW CONSTRUCT THE SCAN (STRONGLY CONSTRAINED AND APPROPRIATELY NORMED) META-GGA
A GGA CONSTRUCTS THE XC ENERGY DENSITY FROM THE LOCAL ELECTRON DENSITY AND ITS GRADIENT. A META-GGA EMPLOYS ALSO THE KINETIC ENERGY DENSITY OF THE KOHN-SHAM ORBITALS.

SCAN WAS CONSTRUCTED TO SATISFY ALL 17 EXACT CONSTRAINTS (MATHEMATICAL PROPERTIES OF THE EXACT FUNCTIONAL) THAT A META-GGA CAN SATISFY.

2015- SCAN FOUND TO BE TYPICALLY MUCH MORE ACCURATE THAN GGA’s OR OTHER META-GGA’s.
THE MATERIALS PROJECT AT BERKELEY IS AN ON-LINE DATABASE OF THE COMPUTED PROPERTIES OF ABOUT 60,000 SOLIDS, USING THE PBE GGA OF DFT. OVER THE COURSE OF MORE THAN A YEAR, IT IS BEING SWITCHED TO THE SCAN META-GGA.

DFT IS NOT JUST A ONE-ELECTRON, MEAN-FIELD, OR WEAK-CORRELATION THEORY.

BETTER APPROXIMATIONS ARE LEADING TO FIRST-PRINCIPLES PREDICTIONS FOR INTERESTING AND CHALLENGING MATERIALS. BUT THERE IS STILL MUCH ROOM FOR FURTHER IMPROVEMENT.
Electronic structure problem

For atoms, molecules, and solids

What atoms, molecules, and solids can exist, and with what properties?

What are the groundstate energies $E$ and electron densities $n/r$?

What are the bond lengths and angles?

$\equiv \equiv$

What are the nuclear vibrations?

How much energy is needed to ionize the system, or to break bonds?
WAVEFUNCTION APPROACH

HAMILTONIAN FOR N ELECTRONS (i=1...N) IN THE PRESENCE OF EXTERNAL POTENTIAL \( V(\mathbf{r}) \):

\[
\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_i \hat{V}(\mathbf{r}_i)
\]

\[
\hat{T} = \sum_i -\frac{1}{2} \mathbf{\hat{p}}_i^2
\]

\[
\hat{V}_{ee} = \sum_{i<j} \frac{1}{\| \mathbf{r}_i - \mathbf{r}_j \|}
\]

Often \( \hat{V}(\mathbf{r}) = \sum E \frac{z_i z_j}{|\mathbf{r}_i - \mathbf{r}_j|} \) = ELECTRON-NUCLEUS ATTRACTION

AND INCLUDES ALSO

\[
\frac{1}{2} \sum_{i<j} \frac{z_i z_j}{|\mathbf{r}_i - \mathbf{r}_j|}
\]

= NUCLEUS-NUCLEUS REPULSION.
3. **Schrödinger Equation for Stationary States**

\[ \hat{H} \psi = E \psi \]

\[ \psi = \psi (\vec{a}_1, \vec{a}_2, \ldots \vec{a}_n) \]

\( \psi \) is normalized: \( \langle \psi | \psi \rangle = 1 \),

and antisymmetric:

\[ \psi (...) \psi (a_i a_j ...) \]

\[ = - \psi (...) \psi (a_j a_i ...) \]

\( E \to \Delta E \)

\[ n(E) = N \prod_{i=1}^{n} s_{\vec{a}_i}^3 \prod_{i<j}^n d_{\vec{a}_i, \vec{a}_j}^3 \]

\[ \left| \psi (\vec{a}_1, \vec{a}_2, \ldots \vec{a}_n) \right|^2 \]
5.

WHY NOT MANY-ELECTRON WAVEFUNCTIONS?

IMAGINE A GRID OF M POINTS IN POSITION SPACE FOR EACH ELECTRON.
WE MUST THEN COMPUTE 4 STORE $M^N$ VALUES OF $\Psi$ (KOHN)

LET $M = 10^2$ (NOT REALLY ENOUGH).
FOR $N=2$, $M^N = 10^4$ IS OK.
FOR $N=10$, $M^N = 10^{20}$ IS NOT OK.

AVOIDING GRIDS, ONE CAN STUDY AT MOST (AND AT GREAT EXPENSE) 10 TO 100 ELECTRONS.

THE DENSITY MATRICES HOWEVER WOULD REQUIRE COMPUTING & STORING ONLY $M$ VALUES.
Hohenberg-Kohn Theorem 1964:
Central theorem of DFT

(1) There exists a functional $F[n]$ of the electron density, such that
the GS energy and density for
$n$ electrons in the presence of
external potential $V(r)$ is

$$E_{gs} = \min_n \left\{ F[n] + \int d^3 r \frac{1}{2} \nabla^2 \psi(r) \psi(r) \right\}.$$  

The minimum is taken over all
positive $n(r)$ such that $\int d^3 r n(r) = n.$

$F[n]$ is universal (independent of $V$);
the problem is to find (approximate
the functional $F[n]$.
(2) THE EXTERNAL POTENTIAL $V(\vec{r})$ \\
AND HENCE THE HAMILTONIAN $\hat{H}$ \\
ARE DETERMINED TO WITHIN AN \\
ADDITIVE CONSTANT BY $\hbar^2/2m$.

PROOF BY LEVY CONSTRAINED SEARCH 1979

$$E_{\text{ee}} = \min_{\vec{\psi}} \langle \vec{\psi} | \hat{H} + \hat{V}_{\text{ee}} + \frac{\hbar^2}{2m} \Delta | \vec{\psi} \rangle$$

$$= \min_{\vec{\psi}} \min_{\vec{\nu} \rightarrow \vec{\nu}} \langle \vec{\nu} | \hat{H} + \hat{V}_{\text{ee}} | \vec{\nu} \rangle$$

$$= \min_{\vec{\nu}} \langle \vec{\nu} | \hat{H} + \hat{V}_{\text{ee}} | \vec{\nu} \rangle$$

$$F[\nu] = \min_{\vec{\nu} \rightarrow \vec{\nu}} \langle \vec{\nu} | \hat{H} + \hat{V}_{\text{ee}} | \vec{\nu} \rangle$$

$$\phi_{\nu} = \text{THAT WAVEFUNCTION YIELDING}$$

$$\text{DENSITY $\rho_{\nu}$ THAT MINIMIZES $\langle \hat{T} + \hat{V} \rangle$}$$
EULER EQUATION FOR $n(F)$:

\[
\delta F[F] + Sd^3 n \delta n \psi(F) - \mu Sd^3 n \delta n = 0
\]

\[
\frac{\delta F}{\delta n(F)} + \psi(F) - \mu = 0 \quad \text{for } GS
\]

\[
\psi(F) = \mu - \frac{\delta F}{\delta n(F)}
\]

FUNCTIONAL DERIVATIVE $\frac{\delta F}{\delta n(F)}$:

\[
\delta F = Sd^3 \left( \frac{\delta F}{\delta n(F)} \right) \delta n(F)
\]

EX:

\[
E_x^{\text{hom}}[n] = -C Sd^3 n^{4/3}(F)
\]

\[
\delta E_x^{\text{hom}}[n] = -C Sd^3 \frac{4}{3} n^{1/3}(F) \delta n(F)
\]

\[
\frac{\delta E_x^{\text{hom}}}{\delta n(F)} = -\frac{4}{3} C n^{1/3}(F)
\]
The constrained search is for understanding, not for calculating!

The exact $F[n]$ requires a constrained search over n-electron wavefunctions, which is impractical.

Approximations for $F[n]$ that are explicit functionals of $n(f)$ are too crude to be very useful.

1965: The Kohn-Sham scheme introduces orbitals that are implicit functionals of the density, and calculates the biggest part of $F[n]$ exactly from these orbitals.
Kohn-Sham non-interacting system:
A fictional non-interacting ground state $\Phi_n$ (usually a single Slater determinant) with the same density $\rho_n$ and chemical potential as the physical interacting ground state $\Psi_n$.

$$\hat{H}_S = \hat{T} + \sum_{i} U_S (\Phi_i)$$

$s =$ single-particle

$$\hat{H}_S \Phi_n = E_n \Phi_n$$

$\Psi_n =$ that noninteracting wave function yielding density $\rho_n$ and minimizing $\langle \Phi \rangle$. 
NON-INTERACTING KINETIC ENERGY

\[ T_s[n] = \langle \Phi_n | \hat{T}^{s} | \Phi_n \rangle \]

\[ F[n] = \langle \Phi_n | \hat{T}^{s} + \hat{V}_{ee} | \Phi_n \rangle = \langle \Phi_n | \hat{T}^{s} + \hat{V}_{ee} | \Phi_n \rangle + E_c[n] \]

CORRELATION ENERGY

\[ E_c[n] = \langle \Phi_n | \hat{V}_{ee} | \Phi_n \rangle - \langle \Phi_n | \hat{V}_{ee} | \Phi_n \rangle \leq 0 \]

\[ \langle \Phi_n | \hat{V}_{ee} | \Phi_n \rangle = U[n] + E_x[n] \]

HARTREE ELECTROSTATIC ENERGY

\[ U[n] = \sum_{n \neq n'} \frac{1}{4 \pi \varepsilon_0} \frac{e^2}{r_{nn'}} \frac{\langle \Phi_n | \hat{r} | \Phi_n \rangle}{r_{nn'}} \]

EXCHANGE ENERGY \( E_x[n] \)

\[ F[n] = \frac{T_s[n] + U[n]}{\text{TREATED EXACTLY}} + \frac{E_c[n]}{\text{SOME APPROX. FOR } E_x + E_c} \]
EULER EQUATIONS

\[
\begin{align*}
\frac{\partial T_0}{\partial x(i)} + u_0(i) &= 0, \\
\frac{\partial T_e}{\partial x(i)} + \frac{\partial u_e}{\partial x(i)} + \frac{\partial E_{xc}}{\partial n(i)} + u_e(i) &= 0,
\end{align*}
\]

\[u_s(i) = u(i) + \frac{\partial^2}{\partial x(i)} + u_e(i) = 0\]

\[u_{xc}(i) = \frac{\partial E_{xc}}{\partial n(i)}\]

SELF-CONSISTENT Kohn-Sham Scheme

\[
\left[-\frac{1}{2} \nabla^2 + V(i) + \frac{\partial^2}{\partial x(i)} + u_e(i) \right] \chi(i) = E \chi(i)
\]

\[n(i) = \frac{\sum_{\alpha} |\chi_{\alpha}(i)|^2}{Z}\]

\[\gamma(i) = \frac{\sum_{\alpha} |\chi_{\alpha}(i)|^2}{2} \left( -\frac{1}{2} \nabla^2 + V(i) \right) \chi(i)\]

THE Kohn-Sham ORBITALS \(\chi(i)\) ARE IMPLICIT FUNCTIONALS OF \(n(i)\).
COUPLING CONSTANT INTEGRAL FOR EXC

LANGRETH + PERDEW 1975

\[ \hat{H}_\lambda = \hat{T} + 2\hat{V}_{ee} + \frac{3}{2} \sum_i \hat{v}_\lambda(\vec{r}_i) \]

Adjust \( v_\lambda(\vec{r}) \) to hold the GS density fixed at its \( \lambda=1 \) value.

\( \lambda=1 \): REAL INTERACTING SYSTEM

\[ v_\lambda(\vec{r}) = \psi(\vec{r}) \]

\( \lambda=0 \): Kohn-Sham non-interacting system

\[ \psi^0 \] = that wavefunction yielding density \( \psi(\vec{r}) \) that minimizes \( \langle \hat{T} + 2\hat{V}_{ee} \rangle \)

\[ \psi^1 \rightarrow \psi \], \[ \psi^0 = \phi \]
\[ E_{xc} [n] = \langle \frac{1}{2} \alpha_n + \beta_n \rangle \]
\[ - \langle \alpha_n \rho_0 \beta_n \rangle - U \langle \beta_n \rangle \]
\[ = \langle \alpha_n \rho_0 \beta_n \rangle - U \langle \beta_n \rangle \]
\[ = \int_0^1 \rho_0 \beta_n \beta_n \langle \beta_n \rangle - U \langle \beta_n \rangle \]

\text{By Hellmann-Feynman}

\[ \langle \alpha_n \beta_n \rangle = \frac{1}{2} \rho_0 \beta_n \beta_n \frac{\rho_0^2 \langle \alpha_n \beta_n \rangle}{1 + \rho_0^2} \]

\text{where}

\[ \rho_2 (\hat{r}, \hat{r}) = N (N-1) \frac{\beta_n}{\hat{r}} \sum_{\beta_n} \frac{\beta_n \beta_n \beta_n}{\hat{r}^2} \]

\[ = \text{two-particle density matrix} \]
$\rho^2(r, \vec{r}) = \text{JOINT PROBABILITY DENSITY}$

$= n(r) \left[ n(r) + n_{xc}(r, \vec{r}) \right]$ 

$Sd^2 \cdot Sd^2 \cdot \rho^2 (r, \vec{r}) = N/N$ 

$Sd^2 \cdot Sd^2 \cdot n(r) \cdot n(r) = N(N)$ 

so $Sd^2 \cdot n_{xc}^2 (r, \vec{r}) = -1 \quad \text{SUM RULE}$

$n_{xc}^2 (r, \vec{r}) = \text{DENSITY AT } \vec{r} \text{ OF THE XC HOLE AROUND AN ELECTRON AT } \vec{r}$

around an electron at $\vec{r}$, one electron is missing from the space $\vec{r} \neq \vec{r}'$.

$E_{xc}(N) = S_0^2 \cdot \frac{1}{2} Sd^2 \cdot Sd^2 \cdot n(r) \cdot n_{xc}^2 (r, \vec{r}) \frac{1}{T \cdot \vec{r} / \vec{r}}$
$E_x$ can be expressed as a peculiar integral of occupied orbitals:

$$
\eta_x (\eta_x \eta_x) = \eta_{xc}^{(n=0)} (\eta_x \eta_x)
$$

$$
= - \frac{1}{\hbar \omega} \sum_\nu \nu c_{\nu \nu} \phi_{\nu \nu}^2
$$

where

$$
\rho_{\nu \nu} (\eta_x \eta_x) = \frac{1}{\hbar \omega} \phi_{\nu \nu}^2
$$

= Kohn-Sham one-particle density matrix

**Exact Constraints:** We know many exact constraints on the hole (such as the sum rule) or on the $xc$ energy.
EX: UNIFORM DENSITY SCALING OF $E_X [n]$

LEVY & PERDEW

FOR ANY POSITIVE SCALE PARAMETER $\alpha$, DEFINE A SCALED DENSITY

$$n_\alpha (r) = \alpha^3 n (\alpha r)$$

$$\frac{n_{\alpha n}}{n_{n n}} = \alpha^2$$

When

$$n (r) \rightarrow n_\alpha (r),$$
$$n_\alpha (r) \rightarrow \alpha^3 n (\alpha r),$$
so

$$E_X [n_\alpha] = \alpha^2 E_X [n]$$

HIGH-DENSITY LIMIT: $\alpha \rightarrow \infty$

$$E_C [n_\alpha] \rightarrow \text{CONSTANT} \quad \text{(NO KS DEGENER}}$$

$E_X$ DOMINATES $E_C$
Many other exact constraints on $\pi_{xc}(n)$, $\phi(\hat{r}, \hat{v})$, or $E_{xc}(n)$ have been derived. These constraints have been used to construct approximations to $E_{xc}(n)$, without (or with) fitting to data.

Fully nonempirical:

Local density approximation
PBE generalized gradient approx.
TPSS meta-generalized gradient approximation
WE CAN CONSTRUCT THE EXACT $E_x$ FROM KONOH-SHAM ORBITALS (AS IN OEP), BUT BONDS ARE DESCRIBED BETTER WHEN WE MAKE THE SAME LOCAL OR SEMI-LOCAL APPROXIMATION FOR $E_x$ AND FOR $E_C$. THAT IS BECAUSE $\eta_{xc}(\mathbf{r},\mathbf{r}^\prime)$ IS TYPICALLY DEEPER, MORE SHORT-RANGED IN $(\mathbf{r}^\prime-\mathbf{r})$, AND THUS MORE SEMI-LOCAL THAN IS $\eta_x(\mathbf{r},\mathbf{r}^\prime)$. 
SIMPLEST DENSITY FUNCTIONAL:
LOCAL DENSITY APPROXIMATION

\[ E_{xc}^{\text{LM}}[n] = S d^3 x \n(\n(x)) \Sigma_{\text{H}}^{\text{Hnf}}(n(x)) \]

\[ \Sigma_{\text{H}}^{\text{Hnf}}(n) = \infty \text{ ENERGY PER ELECTRON} \]

FOR AN ELECTRON GAS OF UNIFORM DENSITY \( n \).

EXACT FOR A UNIFORM DENSITY.
CORRECTIONS FOR A SLOWLY-VARYING DENSITY \( \sim |\n'|^2 \).

\[ \Sigma_{\text{xc}}^{\text{LM}}(n'/n) = \Sigma_{\text{xc}}^{\text{Hnf}}(n'; \lfloor n'/n \rfloor) \]

SATISFIES SUM RULE AND SEVERAL OTHER EXACT CONSTRAINTS,
INCLUDING SCALING FOR \( x \).
JACOB'S LADDER OF DENSITY FUNCTIONAL APPROXIMATIONS

\[ E_x = \sum \frac{1}{2} \langle n, d \rangle \] 

\[ z(1) = \frac{1}{2} \sum_{\alpha} |\phi_{\alpha}|^2 = \text{positive} \]

HEAVEN OF CHEMICAL ACCURACY

HARTREE WORLD

SAMPLE/LCK

GENERALIZED RPA

HYPER-DCA

REMA-GIA

GGA

LDA
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