

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, NANOSTRUCTURES, 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 SELFCONSISTENT ONE-ELECTRON SCHRÖDINGER 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-
INTEGER 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.

SCAN OFTEN PREDICTS THE SMALL ENERGY DIFFERENCES BETWEEN DIFFERENT PHASES OF COMPLEX MATERIALS (E.G., WATER) AND STRONGLY-CORRELATED MATERIALS (E.G., THE POLYMORPHS OF MnO_2 , THE BAND GAPS AND STRIPES IN CUPRATE HIGH-TEMPERATURE SUPERCONDUCTOR MATERIALS).

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.

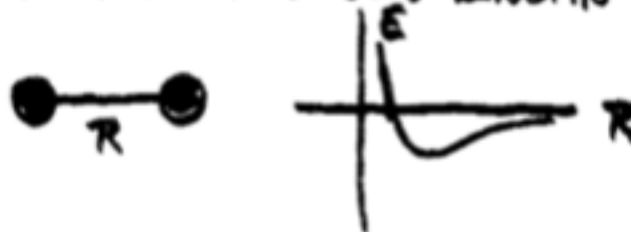
1.

ELECTRONIC STRUCTURE PROBLEM
FOR ATOMS, MOLECULES, & SOLIDS

WHAT ATOMS, MOLECULES, & SOLIDS
CAN EXIST, AND WITH WHAT
PROPERTIES?

WHAT ARE THE GROUNDSTATE ENERGIES
 E AND ELECTRON DENSITIES $n(r)$?

WHAT ARE THE BOND LENGTHS & ANGLES?



WHAT ARE THE NUCLEAR VIBRATIONS?

HOW MUCH ENERGY IS NEEDED TO
IONIZE THE SYSTEM, OR TO BREAK
BONDS?

WAVEFUNCTION APPROACH

HAMILTONIAN FOR N ELECTRONS ($i=1\dots N$)
IN THE PRESENCE OF EXTERNAL POTENTIAL

$V(\vec{r})$:

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_i V(\vec{r}_i)$$

$$\hat{T} = \sum_i -\frac{1}{2} \nabla_i^2$$

$$\hat{V}_{ee} = \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$\text{OFTEN } V(\vec{r}) = \sum_B \frac{-Z_B}{|\vec{r} - \vec{R}_B|}$$

= ELECTRON-NUCLEUS ATTRACTION,

AND E INCLUDES ALSO

$$\frac{1}{2} \sum_B \sum_{B' \neq B} \frac{Z_B Z_{B'}}{|\vec{R}_B - \vec{R}_{B'}|}$$

= NUCLEUS-NUCLEUS REPELSION.

3.

SCHRÖDINGER EQUATION FOR STATIONARY STATES

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

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

Ψ IS NORMALIZED: $\langle \Psi | \Psi \rangle = 1$,

AND ANTISYMMETRIC:

$$\begin{aligned} \Psi(\dots \vec{r}_i \sigma_i \dots \vec{r}_j \sigma_j \dots) \\ = -\Psi(\dots \vec{r}_j \sigma_j \dots \vec{r}_i \sigma_i \dots) \end{aligned}$$

$E \rightarrow \Delta E$

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

5.

WHY NOT MANY-ELECTRON WAVEFUNCTIONS?

IMAGINE A GRID OF M POINTS
IN POSITION SPACE FOR EACH ELECTRON.
WE MUST THEN COMPUTE & STORE
 M^N VALUES OF Ψ . (KOHU)

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 $n(r)$ HOWEVER WOULD
REQUIRE COMPUTING & STORING
ONLY M VALUES.

6.

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 $v(\vec{r})$ IS

$$E_{GS} = \min_n \left\{ F[n] + \int d\vec{r} v(\vec{r}) n(\vec{r}) \right\}.$$

THE MINIMUM IS TAKEN OVER ALL POSITIVE $n(\vec{r})$ SUCH THAT $\int d\vec{r} n(\vec{r}) = N$.

$F[n]$ 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 $n(\vec{r})$.

PROOF BY LEVY CONSTRAINED SEARCH M79

$$\begin{aligned}
 E_{GS} &= \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_i v(\vec{r}_i) | \Psi \rangle \\
 &= \min_n \min_{\Psi \rightarrow n} \left\{ \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int d^3r v(\vec{r}) n(\vec{r}) \right\} \\
 (i) \quad &= \min_n \left\{ F[n] + \int d^3r v(\vec{r}) n(\vec{r}) \right\}
 \end{aligned}$$

$$\begin{aligned}
 F[n] &= \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \\
 &= \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle
 \end{aligned}$$

Ψ_n = THAT WAVEFUNCTION YIELDING
DENSITY $n(\vec{r})$ THAT MINIMIZES $\langle \hat{T} + \hat{V}_{ee} \rangle$

EULER EQUATION FOR $n(\vec{r})$:

$$\delta \left\{ F[n] + \int d^3r n(\vec{r}) \psi(\vec{r}) - \mu \int d^3r n(\vec{r}) \right\} = 0$$

$$(2) \quad \left. \begin{aligned} \frac{\delta F}{\delta n(\vec{r})} + \psi(\vec{r}) - \mu &= 0 \\ \psi(\vec{r}) &= \mu - \frac{\delta F}{\delta n(\vec{r})} \end{aligned} \right\} \begin{array}{l} \text{FOR GS} \\ n(\vec{r}) \end{array}$$

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

$$\delta F \equiv \int d^3r \left(\frac{\delta F}{\delta n(\vec{r})} \right) \delta n(\vec{r}) .$$

$$\text{EX: } E_x^{\text{LDA}}[n] = -C \int d^3r n^{4/3}(\vec{r})$$

$$\delta E_x^{\text{LDA}}[n] = -C \int d^3r \frac{4}{3} n^{1/3}(\vec{r}) \delta n(\vec{r})$$

$$\frac{\delta E_x^{\text{LDA}}}{\delta n(\vec{r})} = -\frac{4}{3} C n^{1/3}(\vec{r})$$

9.

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 $n(\vec{r})$ 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 NONINTERACTING GROUND STATE Φ_n (USUALLY A SINGLE SLATER DETERMINANT) WITH THE SAME DENSITY $n(r)$ AND CHEMICAL POTENTIAL AS THE PHYSICAL INTERACTING GROUND STATE Ψ_n .

$$\hat{H}_S = \hat{T} + \sum_i v_S(r_i)$$

$S =$ single-particle

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

$\Phi_n =$ THAT NONINTERACTING WAVEFUNCTION YIELDING DENSITY $n(r)$ AND MINIMIZING $\langle \hat{T} \rangle$.

NON-INTERACTING KINETIC ENERGY

$$T_S [n] = \langle \Phi_n | \hat{T} | \Phi_n \rangle$$

$$\begin{aligned} F[n] &= \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle \\ &= \langle \Phi_n | \hat{T} + \hat{V}_{ee} | \Phi_n \rangle + E_c [n] \end{aligned}$$

CORRELATION ENERGY

$$\begin{aligned} E_c [n] &= \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle - \langle \Phi_n | \hat{T} + \hat{V}_{ee} | \Phi_n \rangle \\ &\leq 0. \end{aligned}$$

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

HARTREE ELECTROSTATIC ENERGY

$$U [n] = \frac{1}{2} \iint \rho(\mathbf{r}) \rho(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

EXCHANGE ENERGY $E_x [n]$

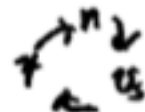
$$F[n] = \underbrace{T_S [n] + U [n]}_{\text{TREATED EXACTLY}} + \underbrace{E_{xc} [n]}_{\text{SOME APPROX. FOR } E_x + E_c}$$

EULER EQUATIONS

$$\left. \begin{aligned} \frac{\delta T_S}{\delta n(\vec{r})} + v_S(\vec{r}) &= \mu \\ \frac{\delta T_S}{\delta n(\vec{r})} + \frac{\delta U}{\delta n(\vec{r})} + \frac{\delta E_{xc}}{\delta n(\vec{r})} + v(\vec{r}) &= \mu \end{aligned} \right\} \text{SAME SOLUTION}$$

$$v_S(\vec{r}) = v(\vec{r}) + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + v_{xc}(n; \vec{r})$$

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



SELF-CONSISTENT KOHN-SHAM SCHEME

$$\left[-\frac{1}{2} \nabla^2 + v(\vec{r}) + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + v_{xc}(n; \vec{r}) \right] \psi_a(\vec{r}) = \epsilon_a \psi_a(\vec{r})$$

$$n(\vec{r}) = \sum_a^{\text{occ}} |\psi_a(\vec{r})|^2$$

$$T_S[n] = \sum_a^{\text{occ}} \int d\vec{r} \psi_a^*(\vec{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_a(\vec{r})$$

THE KOHN-SHAM ORBITALS $\psi_a(\vec{r})$ ARE IMPLICIT FUNCTIONALS OF $n(\vec{r})$.

COUPLING CONSTANT INTEGRAL FOR E_{xc}
LANGRATH + PERDEW 1975

$$\hat{H}_\lambda = \hat{T} + \lambda \hat{V}_{ee} + \sum_i v_\lambda(\vec{r}_i)$$

ADJUST $v_\lambda(\vec{r})$ TO HOLD THE GS DENSITY
FIXED AT ITS $\lambda=1$ VALUE.

$\lambda=1$: REAL INTERACTING SYSTEM

$$v_\lambda(\vec{r}) = v(\vec{r}).$$

$\lambda=0$: KOHN-SHAM NON-INTERACTING SYSTEM

Ψ_n^λ = THAT WAVEFUNCTION YIELDING DENSITY
 $n(\vec{r})$ THAT MINIMIZES $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$.

$$\Psi_n^1 = \Psi_n, \quad \Psi_n^0 = \Phi_n$$

$$\begin{aligned}
 E_{xc}[n] &= \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle \\
 &= \langle \Psi_n | \hat{T} | \Psi_n \rangle - U[n] \\
 &= \left. \langle \Psi_n^\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_n^\lambda \rangle \right|_{\lambda=0} - U[n] \\
 &= \int_0^1 d\lambda \frac{d}{d\lambda} \langle \Psi_n^\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_n^\lambda \rangle - U[n] \\
 &= \int_0^1 d\lambda \langle \Psi_n^\lambda | \hat{V}_{ee} | \Psi_n^\lambda \rangle - U[n] \\
 &\quad \text{BY HELLMANN-FEYNMAN}
 \end{aligned}$$

$$\langle \Psi_n^\lambda | \hat{V}_{ee} | \Psi_n^\lambda \rangle = \frac{1}{2} \int d\vec{r} \int d\vec{r}' \frac{\rho_2^\lambda(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|}$$

WHERE

$$\begin{aligned}
 \rho_2^\lambda(\vec{r}, \vec{r}') &= N(N-1) \sum_{i_1} \dots \sum_{i_N} \int d\vec{r}_3 \dots d\vec{r}_N \\
 &\quad |\Psi_n^\lambda(\vec{r}, i_1, \vec{r}', i_2, \vec{r}_3, \dots, \vec{r}_N, i_N)|^2 \\
 &= \text{TWO-PARTICLE DENSITY MATRIX}
 \end{aligned}$$

15.

$$\rho_2^2(\vec{r}, \vec{r}') = \text{JOINT PROBABILITY DENSITY}$$

$$= n(\vec{r}) \left[n(\vec{r}') + n_{xc}^2(\vec{r}, \vec{r}') \right]$$

$$\int d\vec{r} \int d\vec{r}' \rho_2(\vec{r}, \vec{r}') = N(N-1)$$

$$\int d\vec{r} \int d\vec{r}' n(\vec{r}) n(\vec{r}') = N(N)$$

$$\text{SO } \int d\vec{r}' n_{xc}^2(\vec{r}, \vec{r}') = -1 \quad \text{SUM RULE}$$

$n_{xc}^2(\vec{r}, \vec{r}')$ = DENSITY AT \vec{r}' OF THE XC HOLE AROUND AN ELECTRON AT \vec{r} . AROUND AN ELECTRON AT \vec{r} , ONE ELECTRON IS MISSING FROM THE SPACE $\vec{r}' \neq \vec{r}$.

$$E_{xc}[N] = \int_0^1 dx \frac{1}{2} \int d\vec{r} \int d\vec{r}' n(\vec{r}) \frac{n_{xc}^2(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|}$$

E_x CAN BE EXPRESSED AS A POLE
INTEGRAL OF OCCUPIED ORBITALS:

$$n_x(r, \bar{r}) = n_{xc}^{2=0}(r, \bar{r})$$

$$= -\frac{1}{n(r)} \sum_c |\rho_c(r, \bar{r})|^2$$

$$\text{WHERE } \rho_c(r, \bar{r}) = \sum_{\alpha} z_{\alpha c}^{\dagger}(r) z_{\alpha c}(r)$$

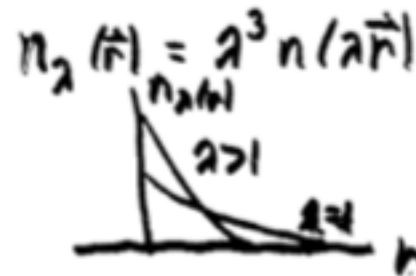
= KOHN-SHAM ONE-PARTICLE
DENSITY MATRIX

EXACT CONSTRAINTS: WE KNOW MANY
EXACT CONSTRAINTS ON THE HOLE
(SUCH AS THE SUM RULE) OR ON THE
XC ENERGY.

17.

EX: UNIFORM DENSITY SCALING OF $E_x [n]$
 LEVY + TAIL

FOR ANY POSITIVE SCALE PARAMETER λ ,
 DEFINE A SCALED DENSITY



WHEN $n(\vec{r}) \rightarrow n_\lambda(\vec{r})$,
 $\sigma_\lambda(\vec{r}) \rightarrow \lambda^{3/2} \sigma(\lambda\vec{r})$,
 SD

$$E_x [n_\lambda] = \lambda E_x [n]$$

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

$E_c [n_\lambda] \rightarrow \text{CONSTANT}$ (NOXS DEGENERATION)

E_x DOMINATES E_c

MANY OTHER EXACT CONSTRAINTS
 ON $\pi_{xc}^2(\mathbf{r}, \hat{\mathbf{r}})$ 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 NUMERICAL :

LOCAL DENSITY APPROXIMATION

PBE GENERALIZED GRADIENT APPROX.

TPSS META-GENERALIZED GRADIENT
 APPROXIMATION

WE CAN CONSTRUCT THE EXACT $E_x[\omega]$ FROM Kohn-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 $n_{xc}^2(r, r')$ IS TYPICALLY DEEPER, MORE SHORT-RANGED IN $|r-r'|$, AND THUS MORE SEMI-LOCAL THAN IS $n_x(r, r')$.

SIMPLEST DENSITY FUNCTIONAL :

LOCAL DENSITY APPROXIMATION

$$E_{xc}^{LDA}[N] = \int d^3r n(r) \epsilon_{xc}^{unif}(n(r))$$

$\epsilon_{xc}^{unif}(n) =$ XC ENERGY PER ELECTRON
FOR AN ELECTRON GAS OF UNIFORM
DENSITY n .

EXACT FOR A UNIFORM DENSITY.

CORRECTIONS FOR A SLOWLY-VARYING
DENSITY $\sim |\nabla n|^2$.

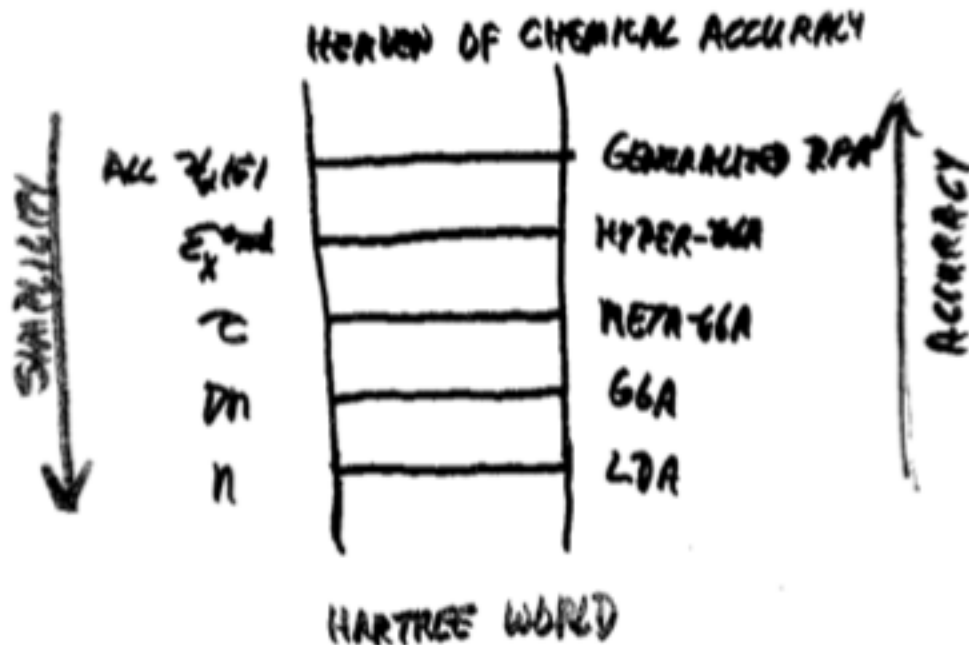
$$\gamma_{xc}^{LDA}(r/\bar{r}) = \gamma_{xc}^{unif}(n(r); |r/\bar{r}|)$$

SATISFIES SUM RULE AND SEVERAL
OTHER EXACT CONSTRAINTS,
INCLUDING SCALING FOR λ .

JACOB'S LADDER OF DENSITY FUNCTIONAL APPROXIMATIONS

$$E_{xc} = \int d\mathbf{r} f(n, \rho n, \tau, \dots)$$

$$\tau(\mathbf{r}) = \sum_{\alpha} \frac{\psi_{\alpha}^2}{2} |\nabla \psi_{\alpha}|^2 = \text{POSITIVE KE DENSITY}$$



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