DENSITY FUNCTIONAL THEORY FOR NON-THEORISTS

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A TUTORIAL FOR PHYSICAL SCIENTISTS WHO MAY
OR MAY NOT HATE EQUATIONS AND PROOFS

REFERENCES FOR FURTHER READING

KIERON BURKE, THE ABC OF DFT, dft.uci.edu/doc/g1.pdf

ROBERT G. PARR AND WEITAO YANG, DENSITY FUNCTIONAL THEORY OF ATOMS AND MOLECULES (OXFORD U. PRESS, 1989)

JOHN P. PERDEW AND STEFAN KURTH, "DENSITY FUNCTIONALS FOR NON-RELATIVISTIC COULOMB SYSTEMS IN THE NEW CENTURY", in A PRIMER IN DENSITY FUNCTIONAL THEORY (SPRINGER LECTURE NOTES IN PHYSICS 620, 1, 2003)

OUTLINE

I.   WHY SHOULD ANYONE CARE ABOUT GROUND-STATE DENSITY FUNCTIONAL THEORY?

II. WHAT IS KOHN-SHAM GROUND-STATE DENSITY FUNCTIONAL THEORY?

(I.1) WHAT IS THE GROUND STATE OF A MANY-ELECTRON SYSTEM, AND WHY IS IT IMPORTANT FOR UNDERSTANDING AND DESIGNING MATERIALS (ATOMS, MOLECULES, SOLIDS, SURFACES,…) ON THE COMPUTER?

THE GROUND STATE IS THE QUANTUM STATE OF LOWEST ENERGY FOR THE ELECTRONS, AND THE EQUILIBRIUM STATE AT ABSOLUTE ZERO TEMPERATURE.

EVEN AT ROOM TEMPERATURE, THE PROPERTIES OF A MATERIAL MAY BE CLOSE TO THOSE OF THE GROUND STATE, SINCE THE THERMAL ENERGY kT =0.03 eV IS MUCH LESS THAN OTHER TYPICAL ENERGIES LIKE THE FERMI ENERGY OF A METAL (SEVERAL eV).

THE NUCLEI ARE MUCH HEAVIER AND SLOWER THAN THE ELECTRONS. SO THE ELECTRONS ARE NEARLY IN A GROUND STATE FOR EACH SET OF NUCLEAR POSITIONS. THE NUCLEAR MOTION CAN OFTEN BE IGNORED, OR TREATED CLASSICALLY VIA NEWTON'S LAWS.

(I.2) WHAT GROUND-STATE PROPERTIES ARE MOST RELEVANT TO EXPERIMENT?

THE GROUND-STATE TOTAL ENERGY E (MEASURABLE BY TOTAL IONIZATION)

CHANGES IN E DUE TO PARTIAL IONIZATION, ATOMIZATION, CHEMICAL REACTION, STRUCTURAL CHANGE, ETC. (OBERVABLE BY SPECTROSCOPY OR CALORIMETRY)

THE ENERGY SURFACE $E(\vec{R}_1, \vec{R}_2, ..., \vec{R}_{N_n})$ FOR A SYSTEM WITH KNOWN NUCLEI AT POSITIONS $\vec{R}_1, \vec{R}_2, ..., \vec{R}_{N_n}$

THE GROUND-STATE STRUCTURE OR GEOMETRY THAT MINIMIZES THE ENERGY SURFACE: SHAPE OF A MOLECULE, CRYSTAL STRUCTURE OF A SOLID (OBSERVABLE BY X-RAY SCATTERING, ETC.)

RELATIVE STABILITIES OF DIFFERENT STRUCTURES

VIBRATIONAL FREQUENCIES OF THE NUCLEI (TREATED AS CLASSICAL PARTICLES WITH POTENTIAL ENERGY $E(R_1, \overline{R}_2, ..., \overline{R}_{N_n})$)

AB INITIO MOLECULAR DYNAMICS OF THE NUCLEI, E.G., IN LIQUIDS.

THE FUNDAMENTAL BAND GAP OF AN INSULATING SOLID

GAP $= I - A$ (DIFFERENCES OF GROUND-STATE ENERGIES)

$I =$ FIRST IONIZATION ENERGY

$A =$ FIRST ELECTRON AFFINITY

THE ELECTRON DENSITY $n(r)$ (NUMBER OF ELECTRONS PER UNIT VOLUME AT A POINT) AND THE SPIN DENSITIES $n_\uparrow(r)$ AND $n_\downarrow(r)$

(OBSERVABLE BY SCATTERING OR BY MAGNETISM)

(I.3) CAN WE COMPUTE AND PREDICT THESE PROPERTIES FROM CORRELATED WAVEFUNCTIONS?

FOR A SYSTEM OF *N* ELECTRONS IN A KNOWN EXTERNAL POTENTIAL (E.G., THE COULOMB ATTRACTION OF THE ELECTRONS TO THE NUCLEI), WE KNOW THE FULL NON-RELATIVISTIC HAMILTONIAN FOR THE ELECTRONS, INCLUDING THE COULOMB REPULSION BETWEEN ANY PAIR OF ELECTRONS.

IN PRINCIPLE, WE HAVE TO FIND THE EIGENSTATE WITH THE LOWEST ENERGY EIGENVALUE (THE GROUND-STATE ENERGY *E*). SINCE THE ELECTRONS ARE FERMIONS, THE EIGENSTATES HAVE TO BE ANTISYMMETRIC UNDER EXCHANGE OF ANY TWO ELECTRONS. THE ELECTRON SPIN DENSITIES CAN BE FOUND BY SQUARING THE WAVEFUNCTION AND INTEGRATING OR SUMMING OVER ALL ARGUMENTS OTHER THAN $\vec{r}$ AND $\sigma = \uparrow \, or \downarrow$

THIS IS EASY FOR N=1, AND DO-ABLE AT INCREASING COST FOR N UP TO ABOUT 50. THE PROBLEM IS THAT THE COULOMB REPULSIONS COUPLE THE MOTIONS OF THE ELECTRONS IN A CORRELATED WAVEFUNCTION $\Psi(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2, ..., \vec{r}_N, \sigma_N)$ THAT HAS "TOO MANY ARGUMENTS".

THE CORRELATED WAVEFUNCTION METHODS OF QUANTUM CHEMISTRY CAN BE VERY ACCURATE (IF SLOW) FOR ATOMS AND SMALL MOLECULES.

BUT WE NEED A COMPUTATIONALLY MORE EFFICIENT WAY TO FIND THE GROUND-STATE ENERGY AND ELECTRON DENSITY, ESPECIALLY FOR:

LARGE OR BIOLOGICAL MOLECULES, AND SOLIDS

HIGH-THROUGHPUT SEARCHES OVER MANY COMPUTED MATERIALS, TO FIND THOSE WITH THE MOST PROMISING PROPERTIES OR FUNCTIONALITIES (AS IN THE MATERIALS GENOME INITIATIVE OR MGI). (WE ARE AN MGI EFRC.)

AB INITIO MOLECULAR DYNAMICS (USING DENSITY FUNCTIONAL THEORY TO FIND THE FORCES ON THE NUCLEI)

TRANSITION TO PART II: DENSITY FUNCTIONAL THEORY IS A COMPUTATIONALLY-EFFICIENT ALTERNATIVE TO COMPUTE GROUND-STATE PROPERTIES, AND IS THE MOST WIDELY-USED METHOD IN QUANTUM CHEMISTRY, CONDENSED-MATTER PHYSICS, AND MATERIALS SCIENCE

A DENSITY FUNCTIONAL IS A MATHEMATICAL RULE TO ASSIGN A SINGLE NUMBER (E.G., AN ENERGY E) TO A FUNCTION OR DISTRIBUTION (E.G., THE ELECTRON DENSITY $n(\vec{r})$).

AS AN EXAMPLE, THE LOCAL DENSITY APPROXIMATION TO THE EXCHANGE ENERGY IS

$$E_x^{LDA}[n] = C \int d^3 r \{n(\vec{r})\}^{4/3} \qquad C = -(3/4\pi)(3\pi^2)^{1/3}$$

THIS IS DESIGNED TO BE EXACT FOR A SYSTEM OF UNIFORM ELECTRON DENSITY OR ONE IN WHICH THE DENSITY VARIES SLOWLY OVER SPACE.

IN THIS CASE, THE RULE IS EXPLICIT. BUT SOMETIMES IT IS ONLY IMPLICIT, AND PERHAPS NOT EXACTLY COMPUTABLE.

THE CHANGE IN THE FUNCTIONAL DUE TO AN INFINITESIMAL DENSITY VARIATION IS LINEAR IN THAT VARIATION:

$$\delta E_x^{LDA}[n] = \int d^3r [\delta E_x^{LDA} / \delta n(\vec{r})]\delta n(\vec{r})$$

IN THE CASE OF THE LOCAL DENSITY APPROXIMATION FOR EXCHANGE, THE FUNCTIONAL DERIVATIVE IS THE LOCAL DENSITY APPROXIMATION TO THE EXCHANGE POTENTIAL:

$$v_x^{LDA}([n], \vec{r}) = \delta E_x^{LDA} / \delta n(\vec{r}) = \partial [Cn^{4/3}]\partial n = (4/3)Cn^{1/3}$$

(II.1) KOHN-SHAM 1965 THEOREM

TO FIND THE GROUND-STATE ENERGY E AND ELECTRON DENSITY OF N REAL INTERACTING ELECTRONS IN AN EXTERNAL POTENTIAL $v(\vec{r})$, WE IMAGINE A FICTITIOUS SYSTEM OF N NON-INTERACTING ELECTRONS WITH THE SAME GROUND-STATE DENSITY $n(\vec{r})$ IN AN EFFECTIVE EXTERNAL POTENTIAL $v_{KS}([n],\vec{r})$. THEN WE HAVE TO SOLVE THE SELF-CONSISTENT ONE-ELECTRON EQUATIONS

$$[-(1/2)\nabla^2 + v_{KS}([n],\vec{r})]\psi_{i\sigma}(\vec{r}) = \varepsilon_{i\sigma}\psi_{i\sigma}(\vec{r})$$

WHERE

$$v_{KS}([n],\vec{r}) = v(\vec{r}) + \int d^3r' n(\vec{r}')/\left|\vec{r}'-\vec{r}\right| + \delta E_{xc}/\delta n(\vec{r})$$

THE GROUND-STATE DENSITY IS

$$n(\vec{r}) = \sum_{i\sigma} \left| \psi_{i\sigma}(\bar{r}) \right|^2$$

SO WE START WITH A GUESS FOR THE DENSITY, THEN ITERATE THESE EQUATIONS TO SELFCONSISTENCY. FINALLY THE GROUND-STATE ENERGY IS

$$E = T_{KS}[n] + \int d^3 r n(\vec{r}) v(\vec{r}) + U[n] + E_{xc}[n]$$

WHERE

$$T_{KS}[n] = \int d^3 r (1/2) \sum_{i\sigma} \left| \nabla \psi_{i\sigma}(\vec{r}) \right|^2$$

$$U[n] = (1/2) \int d^3 r \int d^3 r' n(\vec{r}) n(\vec{r}') / \left| \vec{r}' - \vec{r} \right|$$

IS KOHN-SHAM THEORY A MEAN-FIELD APPROXIMATION?

KOHN-SHAM THEORY PRODUCES UNCOUPLED ONE-ELECTRON SCHROEDINGER EQUATIONS THAT ARE EASY TO SOLVE, VERY MUCH LIKE HARTREE-FOCK THEORY. BUT THIS IS MISLEADING. IN PRINCIPLE, *ALL* MANY-BODY EFFECTS ON THE TOTAL ENERGY AND ELECTRON DENSITY ARE INCLUDED IN THE EXCHANGE-CORRELATION ENERGY FUNCTIONAL $E_{xc}[n]$ AND ITS FUNCTIONAL DERIVATIVE $\delta E_{xc}/\delta n(\vec{r})$.

THE PROBLEM IS THAT THE KOHN-SHAM THEOREM IS AN EXISTENCE THEOREM. IT TELLS US THAT THESE EXCHANGE-CORRELATION DENSITY FUNCTIONALS EXIST, BUT NOT HOW TO COMPUTE THEM. SO WE HAVE TO MAKE APPROXIMATIONS. BUT AT LEAST WE KNOW THAT WHAT WE ARE APPROXIMATING EXISTS IN PRINCIPLE, AND IS IMPORTANT.

(II.2) WHAT IS THE EXCHANGE-CORRELATION ENERGY?

WE CAN DERIVE FORMALLY EXACT (BUT UNCOMPUTABLE) EXPRESSIONS FOR THE EXCHANGE-CORRELATION ENERGY, WHICH TELL US QUALITATIVELY WHAT IT IS AND WHAT EXACT MATHEMATICAL PROPERTIES IT HAS.

THE EXCHANGE-CORRELATION ENERGY IS BASICALLY THE REDUCTION OF COULOMB REPULSION ENERGY ARISING BECAUSE ELECTRONS AVOID ONE ANOTHER DUE TO THEIR PARTICLE NATURE AND THE PAULI EXCLUSION PRINCIPLE (THE EXCHANGE TERM) AND DUE TO COULOMB FORCES (THE CORRELATION TERM). AS AN ELECTRON MOVES THROUGH THE DENSITY, IT IS SURROUNDED BY AN "EXCHANGE-CORRELATION HOLE" FROM WHICH THE OTHER ELECTRONS ARE PARTLY EXCLUDED. THIS IS LIKE THE "PERSONAL SPACE" AROUND A SHOPPER IN A CROWDED MALL.

THE SIMPLE "LOCAL DENSITY" APPROXIMATION (LDA) TO $E_{xc}[n]$, AND HOW IT BINDS ATOMS TOGETHER

KOHN AND SHAM 1965 PROPOSED THE SIMPLE

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

IN WHICH $\varepsilon_{xc}^{unif}(n)$ IS THE EXCHANGE-CORRELATION ENERGY PER PARTICLE OF AN ELECTRON GAS OF UNIFORM DENSITY (KNOWN FROM ACCURATE QUANTUM MECHANICAL CALCULATIONS). THIS WAS DESIGNED TO BE EXACT FOR A UNIFORM DENSITY OR ONE THAT VARIES SLOWLY OVER SPACE. BUT IT WAS UNEXPECTEDLY USEFUL FOR REAL MOLECULES AND SOLIDS.

NEGLECTING $E_{xc}[n]$ BY SETTING IT TO ZERO PRODUCES UNREALISTICALLY LONG AND WEAK BONDS, BUT INCLUDING IT IN LDA OR BETTER APPROXIMATIONS DESCRIBES REAL BONDS.

$E_{xc}[n]$ IS "NATURE'S GLUE" THAT BINDS ATOMS TOGETHER

WHY? BECAUSE, WHEN ATOMS COME TOGETHER, THERE ARE MORE "OTHER" ELECTRONS THAT CAN AVOID A GIVEN ELECTRON, LEADING TO AN EXTRA REDUCTION OF COULOMB REPULSION ENERGY.

OF COURSE, ALL TERMS IN THE ENERGY FUNCTIONAL CHANGE WHEN ATOMS COME TOGETHER, BUT THE NET CHANGE IS DOMINATED BY THE CHANGE IN $E_{xc}[n]$.

LDA HAS A TENDENCY TO MAKE BINDING ENERGIES TOO LARGE AND BOND LENGTHS TOO SHORT. TO GET A REALLY QUANTITATIVE THEORY OF BONDING IN MOLECULES AND SOLIDS, WE NEED MUCH MORE SOPHISTICATED APPROXIMATIONS TO $E_{xc}[n]$.

(II.3) HOW CAN WE CONSTRUCT BETTER APPROXIMATIONS TO $E_{xc}[n]$, BEYOND LDA?

THE SUCCESS OF LDA WAS UNEXPECTED. IN THE MID 1970'S, IT WAS EXPLAINED BY THE FACT THAT LDA IS BASED ON A MODEL EXCHANGE-CORRELATION HOLE BORROWED FROM THE UNIFORM ELECTRON GAS AND THEREFORE SATISFYING UNIVERSAL EXACT CONDITIONS ON THIS HOLE. EARLY GENERALIZED GRADIENT APPROXIMATIONS (GGA'S)

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

WERE CONSTRUCTED BY SATISFYING THESE HOLE CONSTRAINTS. IN THE 1980'S AND LATER, EXACT CONDITIONS WERE DERIVED ON THE ENERGY FUNCTIONAL ITSELF. THE PERDEW-BURKE-ERNZERHOF (PBE) 1996 GGA WAS CONSTRUCTED TO SATISFY SOME OF THESE EXACT CONSTRAINTS ON THE ENERGY, AND IS STILL WIDELY USED BY ITSELF OR WITH VARIOUS CORRECTIONS

BECAUSE THE EXACT CONDITIONS ARE UNIVERSAL, CONSTRUCTING THE FUNCTIONAL BY SATISFYING THESE EXACT CONSTRAINTS GIVES THE FUNCTIONAL GENUINE PREDICTIVE POWER.

A POPULAR ALTERNATIVE IS TO MAKE A PARAMETRIZED FUNCTIONAL AND FIT ITS PARAMETERS TO DATA SETS OF MOLECULAR OR SOLID-STATE DATA. THIS APPROACH CAN BE ACCURATE FOR SYSTEMS SIMILAR TO THOSE IN THE FITTING SETS, BUT IT IS TOO EMPIRICAL FOR MY TASTE. WHEN WE UNDERSTAND, WE DON'T NEED TO FIT (BUT WE DO HAVE TO WORK HARD TO UNDERSTAND).

WE CAN WRITE THE APPROXIMATE EXCHANGE-CORRELATION ENERGY AS AN INTEGRAL OVER THREE-DIMENSIONAL SPACE:

$$E_{xc}^{approx}[n] = \int d^3 r f^{approx}(n, \nabla n, \tau, ...) \qquad \tau(\vec{r}) = (1/2)\sum_{i\sigma}\left|\nabla \psi_{i\sigma}(\vec{r})\right|^2$$

EACH TIME WE ADD ANOTHER INGREDIENT, WE CAN USE IT TO SATISFY MORE EXACT CONSTRAINTS, AND TO MAKE THE FUNCTIONAL MORE ACCURATE BUT COMPUTATIONALLY MORE EXPENSIVE. THERE ARE FIVE RUNGS ON THIS "JACOB'S LADDER", BUT I WILL FOCUS ON THE THREE LOWEST RUNGS, WHICH ARE ALL COMPUTATIONALLY EFFICIENT BECAUSE THEY USE INGREDIENTS AVAILABLE IN ANY KOHN-SHAM CALCULATION:

FIRST RUNG: LOCAL DENSITY APPROXIMATION (LDA): LOCAL DENSITY $n(\vec{r})$ ONLY.

SECOND RUNG: GENERALIZED GRADIENT APPROXIMATION (GGA): ADDS THE DENSITY GRADIENT $\nabla n(\vec{r})$

THIRD RUNG: META-GGA: ADDS THE POSITIVE ORBITAL KINETIC ENERGY DENSITY

$$\tau(\vec{r}) = (1/2) \sum_{i\sigma} \left| \nabla \psi_{i\sigma}(\vec{r}) \right|^2$$

WHAT IS THE NEW *SCAN* (STRONGLY-CONSTRAINED AND APPROPRIATELY-NORMED) META-GGA, AND WHAT ROLE WILL IT PLAY IN OUR EFRC CALCULATIONS?

(JIANWEI SUN, ADRIENN RUZSINSZKY, AND JOHN P. PERDEW, PHYS. REV. LETTERS, TO APPEAR)

SCAN FOR THE FIRST TIME SATISFIES ALL 17 EXACT CONSTRAINTS THAT A META-GGA CAN, AND IS EXACT OR NEARLY-EXACT FOR SYSTEMS IN WHICH THE EXACT EXCHANGE-CORRELATION HOLE REMAINS CLOSE TO ITS ELECTRON (APPROPRIATE NORMS, SUCH AS RARE-GAS ATOMS).

FOR NEARLY THE COMPUTATIONAL COST OF THE PBE GGA, *SCAN* IS MORE ACCURATE THAN PBE GGA AND PREVIOUS META-GGA'S.

SCAN IS NOT FITTED TO ANY BONDED SYSTEM, BUT IT ACCURATELY PREDICTS COVALENT, METALLIC, AND WEAK BONDS. IN PARTICULAR, *SCAN* CAPTURES THE INTERMEDIATE RANGE OF THE VAN DER WAALS INTERACTION, AND SO DESCRIBES WEAK BONDS BETWEEN FRAGMENTS. THIS IS ESPECIALLY IMPORTANT FOR THE LAYERED MATERIALS, IN WHICH THE LAYERS ARE WEAKLY BONDED TO ONE ANOTHER. IN GRAPHENE, WHERE PBE GGA OVERESTIMATES THE INTERLAYER SPACING BY MAYBE 20%, THE *SCAN* META-GGA OVERESTIMATES IT BY 2%. (*SCAN* STILL NEEDS A SMALL LONG-RANGE vdW CORRECTION.)

MnO_2 IS A LAYERED MATERIAL THAT CATALYSES OXYGEN EVOLUTION IN WATER SPLITTING. PBE (WITH OR WITHOUT HYBRID AND HUBBARD-U CORRECTIONS) PREDICTS THE WRONG GROUND-STATE CRYSTAL STRUCTURE FOR THIS MATERIAL, BUT *SCAN* GETS IT RIGHT, IN HAOWEI PENG''S CALCULATIONS.

WHY DO WE NEED ALL THE RUNGS OF JACOB'S LADDER?

THE LOWER RUNGS (LDA AND PBE GGA) ARE SIMPLER. THE WHOLE LADDER ALLOWS US TO UNDERSTAND WHAT EXACT CONSTRAINTS, APPROPRIATE NORMS, AND INGREDIENTS ARE IMPORTANT IN A PARTICULAR SITUATION.

WE NEED THE THIRD RUNG (*SCAN* META-GGA) FOR COMPUTATIONAL EFFICIENCY. COMPUTATIONAL COST CAN INCREASE STEEPLY ON THE FOURTH RUNG (HYBRID FUNCTIONALS, WHICH ARE ALL TO SOME EXTENT EMPIRICAL, AND SELF-INTERACTION CORRECTIONS) AND EVEN MORE ON THE FIFTH RUNG (RANDOM-PHASE-APPROXIMATION-LIKE APPROACHES).
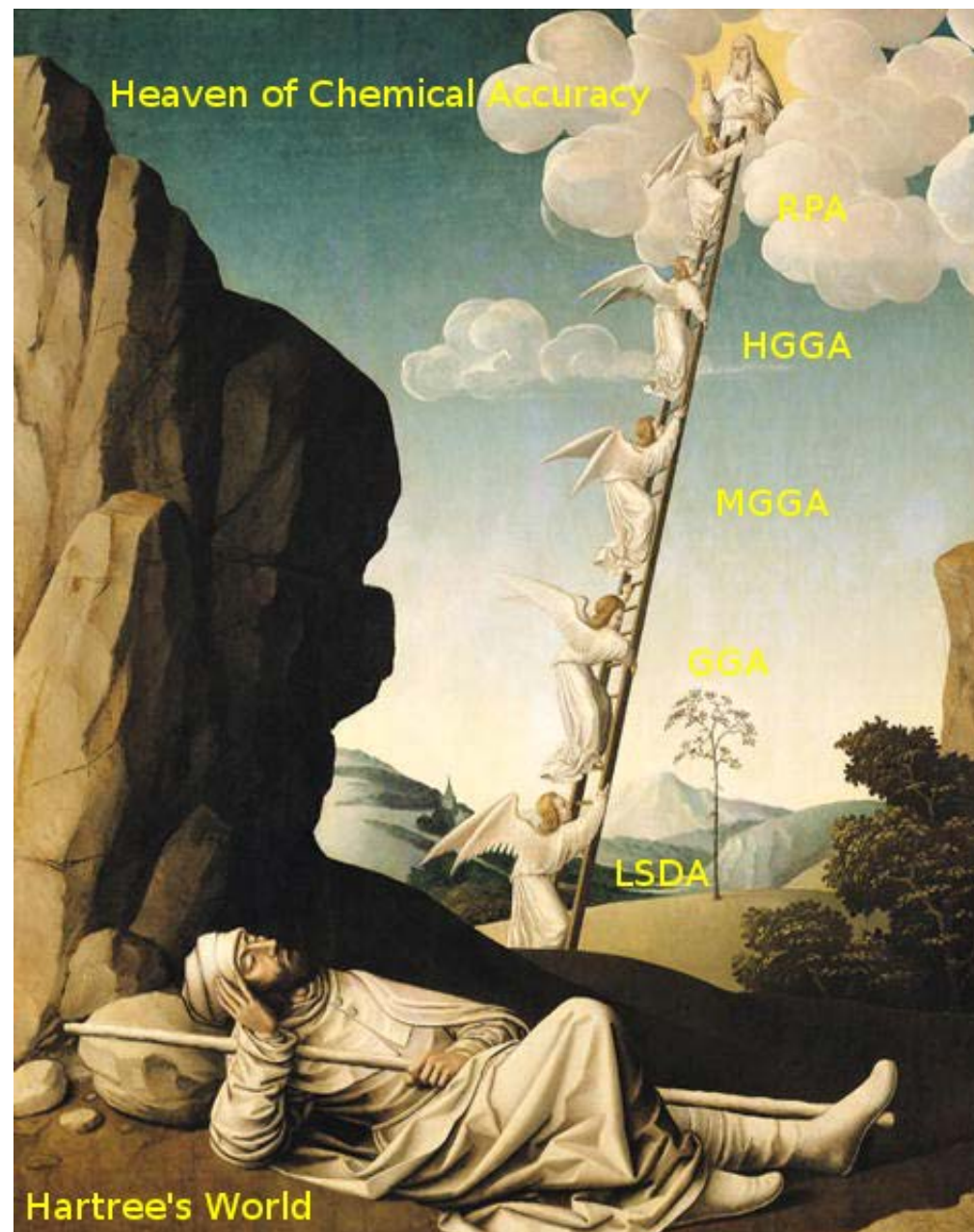
(II.5) SPIN-DENSITY FUNCTIONAL THEORY

THE KOHN-SHAM THEOREM WAS ORIGINALLY PROVED FOR THE TOTAL DENSITY COUPLING TO A SPIN-INDEPENDENT EXTERNAL POTENTIAL. AND FOR SIMPLICITY I HAVE PRESENTED ALL FORMULAS USING THE TOTAL DENSITY. BUT VON BARTH AND HEDIN PROVED THE THEOREMS FOR THE ELECTRON SPIN DENSITIES $n_\uparrow(r)$ & $n_\downarrow(r)$ COUPLING TO A SPIN-DEPENDENT EXTERNAL POTENTIAL. IN PRACTICE, ALL KOHN-SHAM CALCULATIONS ARE DONE IN SPIN-DENSITY FUNCTIONAL THEORY, EVEN IN THE ABSENCE OF A MAGNETIC FIELD COUPLING TO ELECTRON SPIN, FOR TWO REASONS:

(1) TO DESCRIBE MAGNETISM,

(2) TO ACHIEVE HIGHER ACCURACY ON THE SAME RUNG OF JACOB''S LADDER, SINCE A FUNCTIONAL THAT GETS MORE INPUT INFORMATION CAN BE MORE ACCURATE.

(II.6) PITFALLS FOR THE UNWARY

(A) KOHN-SHAM DENSITY FUNCTIONAL THEORY GIVES US ORBITALS, ORBITAL ENERGIES, AND A BAND STRUCTURE FOR A SOLID. THESE QUANTITIES ARE OFTEN USEFUL FOR QUALITATIVE INTERPRETATION. BUT, EVEN IN THE EXACT KOHN-SHAM THEORY, THEY ARE ONLY AUXILIARY QUANTITIES, WITH NO EXACT PHYSICAL INTERPRETATION. IN PARTICULAR, THE EXACT KOHN-SHAM BAND STRUCTURE OF A NEUTRAL SOLID UNDERESTIMATES THE FUNDAMENTAL ENERGY GAP BETWEEN OCCUPIED AND UNOCCUPIED STATES. (ON THE OTHER HAND, EFFECTIVE POTENTIALS THAT ARE NOT MULTIPLICATIVE CAN GIVE MORE PHYSICAL GAPS.)

(B) THE EXACT KOHN-SHAM POTENTIAL IS UNPHYSICAL, AND CAN SHOW INFINITE-RANGED EFFECTS THAT ARE IMPORTANT TO KEEP WELL-SEPARATED ATOMS AND RADICAL MOLECULES ELECTRICALLY NEUTRAL. THE COMPUTATIONALLY-EFFICIENT LDA, GGA, AND META-GGA CAN FAIL FOR SUCH "STRETCHED-BOND RADICALS", REQUIRING A NONLOCAL SELF-INTERACTION CORRECTION.