What Walter Kohn taught me about Density Functional Theory, Life, and the Scientific Process

Ann E. Mattsson
Multi-Scale Science
Sandia National Laboratories, Albuquerque, NM

E-mail: aematts@sandia.gov
Web: http://www.cs.sandia.gov/~aematts/
http://dft.sandia.gov

Kohn Science Symposium
8 December 2016
Santa Barbara, CA, USA

SAND2016-12459 C

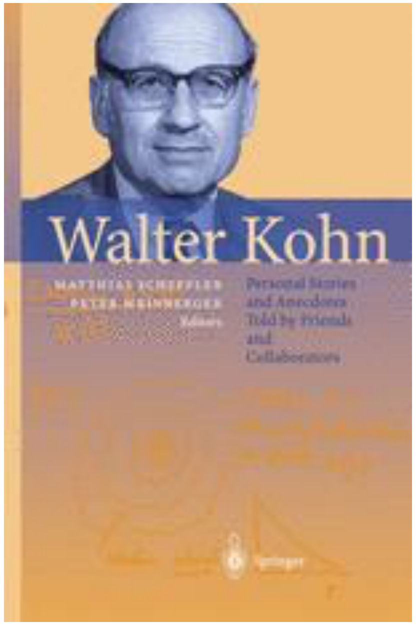
Why am I here?

Short answer: Walter has had a profound influence on my life, and I want to honor him.

I was a full time post-doc with Walter from July 1997 to Dec 1998, and part-time until August 1999 (while also working as an assistant professor at the Royal Institute of Technology in Stockholm, Sweden).

The Nobel Day

Walter was awarded the Nobel Prize in Chemistry on 13 October 1998, and Alex Kamenev, Walter's other post-doc, and me were sent up to ask Walter some organizational questions, like when he wanted to have the press conference (it was pretty clear it should be held in Kohn Hall). Nobody could get through on the phone. Alex suggested we buy flowers and Walter talked about "people coming with red roses" for quite some time after.



Walter Kohn

Matthias Scheffler
Peter Weinberger
Editors

Personal Stories and Anecdotes Told by Friends and Collaborators

Springer

It was an exciting time indeed. Adding to the excitement was that Walter's and my first joint article was published in PRL on October 19, which also happens to be my birthday. Those weeks were definitely some of the most interesting days of my life.

Both Alex and I wrote chapters about this Nobel day in the 2003 book "Walter Kohn: Personal Stories and Anecdotes Told by Friends and Collaborators".

I also got invited to the ceremony! (Since they needed to fill a spot and I was available in Stockholm already).

https://dx.doi.org/10.1007/978-3-642-55609-8

The Scientific Process

These are some of my extraction of life wisdom from Walter's work and life, not necessarily Walter's views.

- Doing the best you can in the areas you are interested in, without thinking too much about what can "pay off", can lead to marvelous results: Walter got the Nobel Prize in Chemistry despite never having taken a chemistry course in his life.
- Walter asked me an endless number of questions before he ever drew a firmer conclusion from what I had done. Every statement I made as being a fact he always found a test that would be able to prove it wrong. The scientific process: You can never prove something correct but only test it endlessly to find a proof that shows it is wrong. And only one proof of failure is enough to revise your world view. This is how science evolves, always finding improvement in the theory so that it explains more facts. You should never close your eyes to facts.
- However, even an imperfect theory is valuable as long as you try to understand why it is failing. But closing your eyes for failure is poor science.
- Simplicity: If a theory cannot be described in simple terms, it is either not a good theory or it is not well understood.

Life

Ann E. Mattsson

- Tolerance: My life and my science are quite entangled and follow the same principles. To me being open to new facts and incorporating them into new thinking about a theory goes hand in hand with assessing new information in society and incorporating that into your thinking. In my view this is tolerance.
- Action: Even though I am not as active in society as I would like to be I greatly admire Walters engagement in various topics outside his main area of expertise. Promoting solar power and developing helpful tools for people with macular degeneration are just two examples I know about but I know he was engaged in many other important things. I hope I will find some issue I can help with in the same way as Walter did.
- Speaking up: I so well remember when Walter, at the Nobel Prize press conference, addressed Austria's congratulation to a "native son".

But what Walter taught me about DFT is what keeps reminding me of him every single day. And for that I am very grateful.

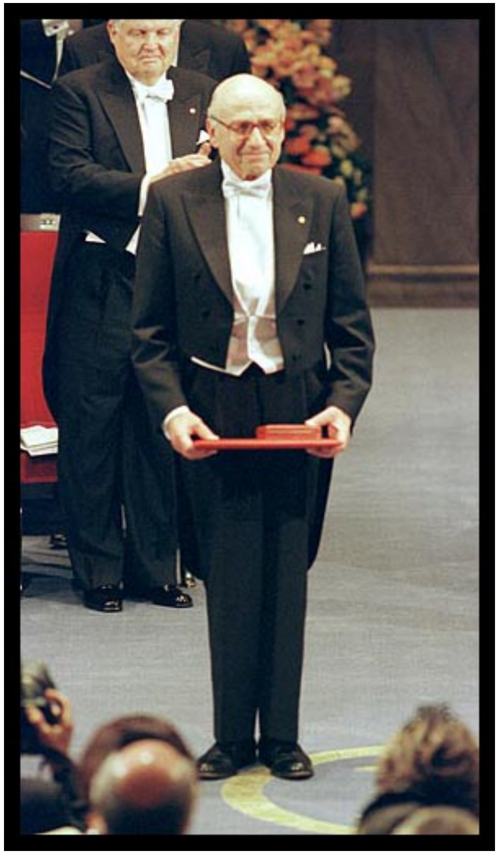
Quantum Mechanics

Dirac (1929)

“ The general theory of quantum mechanics is now almost complete… The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. ”

P.A.M. Dirac, Proc. R. Soc. London Ser. A 123, 714 (1929).

Walter Kohn awarded the Nobel Prize in Chemistry 1998 for Density Functional Theory

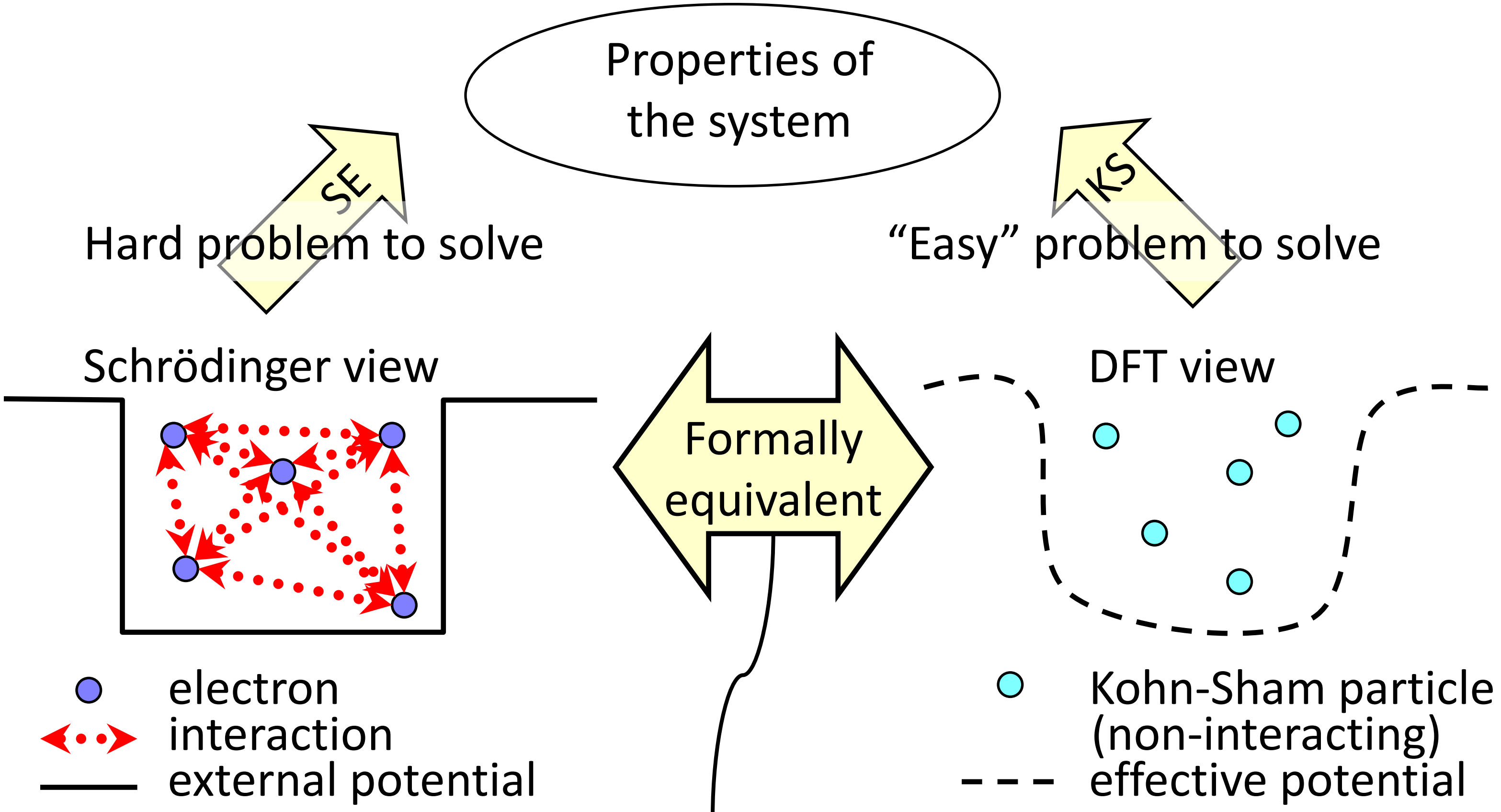


Hohenberg-Kohn theorem:
Phys. Rev. 136, B864 (1964).
The electron density contains all information needed to determine ground state properties of a system.

Kohn-Sham equations:
Phys. Rev. 140, 1133 (1965).
Practical scheme for solving the quantum mechanical problem based on the HK theorem.

DFT versus the Schrödinger Equation

Ann E. Mattsson



Properties of the system

SE

KS

Hard problem to solve

"Easy" problem to solve

Schrödinger view

Formally equivalent

DFT view

● electron
◂··▸ interaction
— external potential

○ Kohn-Sham particle (non-interacting)
- - - effective potential

$$\mathrm{v}_{eff}(\boldsymbol{r}) = \mathrm{v}(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d\boldsymbol{r}' + \frac{\delta E_{xc}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}$$

All many-body effects are included in the effective potential via the Exchange-Correlation functional, $E_{xc}[n(\boldsymbol{r})]$.

Ann E. Mattsson

Kohn-Sham equations:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \mathrm{v}_{eff}(\boldsymbol{r})\right)\psi_\nu(\boldsymbol{r}) = \epsilon_\nu \psi_\nu(\boldsymbol{r}) \quad \nu = 1, 2, \ \ldots., N$$

$$n(\boldsymbol{r}) = \sum_{\nu=1}^{N} |\psi_\nu(\boldsymbol{r})|^2$$

$$\mathrm{v}_{eff}(\boldsymbol{r}) = \mathrm{v}(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d\boldsymbol{r}' + \frac{\delta E_{xc}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}$$

If we had the divine exchange-correlation functional, self-consistently solving these equations would give exactly the same density as the Schrödinger Equation, and thus via the HK theorem, we should be able to extract all information about the system.

Approximations for the exchange-correlation functional

Ann E. Mattsson

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \mathrm{v}_{eff}(\mathbf{r})\right)\psi_\nu(\mathbf{r}) = \epsilon_\nu \psi_\nu(\mathbf{r}) \quad \nu = 1, 2, \;\ldots., N$$

$$n(\mathbf{r}) = \sum_{\nu=1}^{N} |\psi_\nu(\mathbf{r})|^2$$

$$\mathrm{v}_{eff}(\mathbf{r}) = \mathrm{v}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + \boxed{\frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}}$$

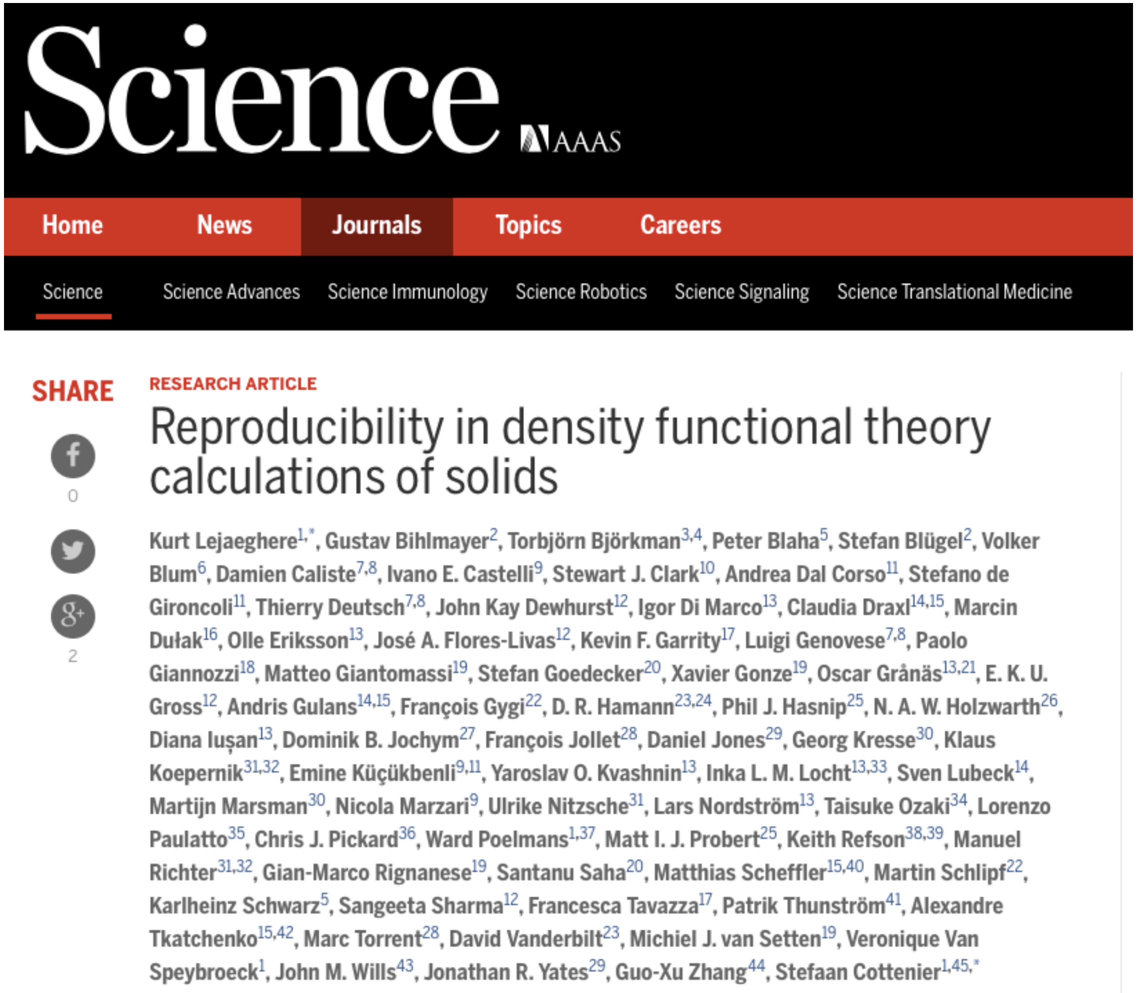
AM05, LDA, GGA, Meta-GGA, Hybrids

The form of the divine exchange-correlation functional is unknown.
We need to find good approximations.

Delta Test

Science 25 Mar 2016: Vol. 351, Issue 6280,
DOI: 10.1126/science.aad3000

Ann E. Mattsson



Science AAAS

Home | News | Journals | Topics | Careers

Science | Science Advances | Science Immunology | Science Robotics | Science Signaling | Science Translational Medicine

SHARE

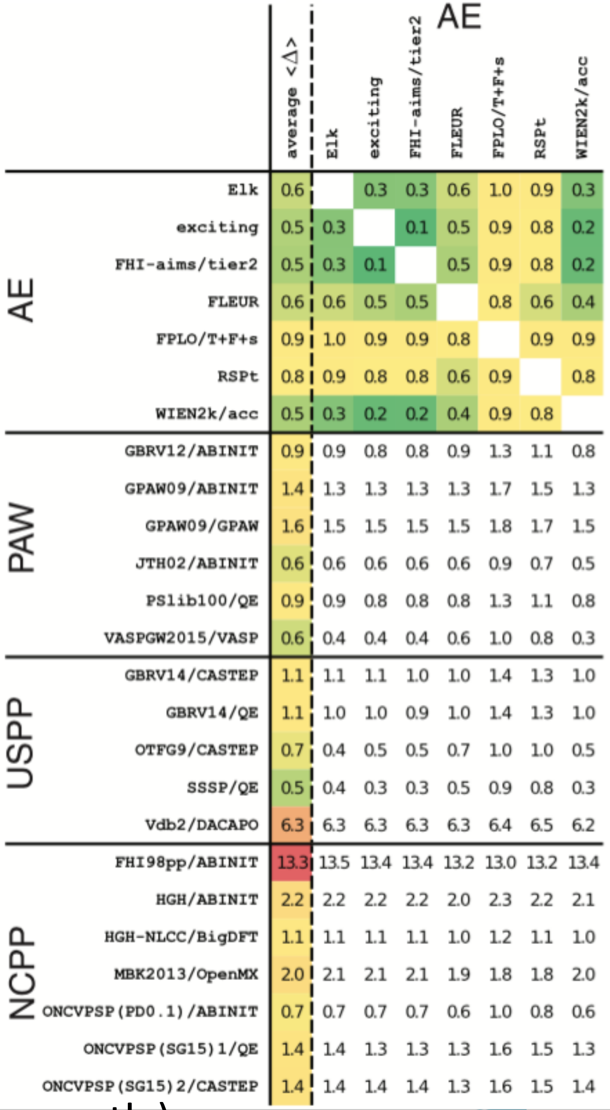
0

2

RESEARCH ARTICLE

Reproducibility in density functional theory calculations of solids

Kurt Lejaeghere[1,*], Gustav Bihlmayer[2], Torbjörn Björkman[3,4], Peter Blaha[5], Stefan Blügel[2], Volker Blum[6], Damien Caliste[7,8], Ivano E. Castelli[9], Stewart J. Clark[10], Andrea Dal Corso[11], Stefano de Gironcoli[11], Thierry Deutsch[7,8], John Kay Dewhurst[12], Igor Di Marco[13], Claudia Draxl[14,15], Marcin Dułak[16], Olle Eriksson[13], José A. Flores-Livas[12], Kevin F. Garrity[17], Luigi Genovese[7,8], Paolo Giannozzi[18], Matteo Giantomassi[19], Stefan Goedecker[20], Xavier Gonze[19], Oscar Grånäs[13,21], E. K. U. Gross[12], Andris Gulans[14,15], François Gygi[22], D. R. Hamann[23,24], Phil J. Hasnip[25], N. A. W. Holzwarth[26], Diana Iuşan[13], Dominik B. Jochym[27], François Jollet[28], Daniel Jones[29], Georg Kresse[30], Klaus Koepernik[31,32], Emine Küçükbenli[9,11], Yaroslav O. Kvashnin[13], Inka L. M. Locht[13,33], Sven Lubeck[14], Martijn Marsman[30], Nicola Marzari[9], Ulrike Nitzsche[31], Lars Nordström[13], Taisuke Ozaki[34], Lorenzo Paulatto[35], Chris J. Pickard[36], Ward Poelmans[1,37], Matt I. J. Probert[25], Keith Refson[38,39], Manuel Richter[31,32], Gian-Marco Rignanese[19], Santanu Saha[20], Matthias Scheffler[15,40], Martin Schlipf[22], Karlheinz Schwarz[5], Sangeeta Sharma[12], Francesca Tavazza[17], Patrik Thunström[41], Alexandre Tkatchenko[15,42], Marc Torrent[28], David Vanderbilt[23], Michiel J. van Setten[19], Veronique Van Speybroeck[1], John M. Wills[43], Jonathan R. Yates[29], Guo-Xu Zhang[44], Stefaan Cottenier[1,45,*]



			AE						
		average <Δ>	Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc
AE	Elk	0.6		0.3	0.3	0.6	1.0	0.9	0.3
	exciting	0.5	0.3		0.1	0.5	0.9	0.8	0.2
	FHI-aims/tier2	0.5	0.3	0.1		0.5	0.9	0.8	0.2
	FLEUR	0.6	0.6	0.5	0.5		0.8	0.6	0.4
	FPLO/T+F+s	0.9	1.0	0.9	0.9	0.8		0.9	0.9
	RSPt	0.8	0.9	0.8	0.8	0.6	0.9		0.8
	WIEN2k/acc	0.5	0.3	0.2	0.2	0.4	0.9	0.8	
PAW	GBRV12/ABINIT	0.9	0.9	0.8	0.8	0.9	1.3	1.1	0.8
	GPAW09/ABINIT	1.4	1.3	1.3	1.3	1.3	1.7	1.5	1.3
	GPAW09/GPAW	1.6	1.5	1.5	1.5	1.5	1.8	1.7	1.5
	JTH02/ABINIT	0.6	0.6	0.6	0.6	0.6	0.9	0.7	0.5
	PSlib100/QE	0.9	0.9	0.8	0.8	0.8	1.3	1.1	0.8
	VASPGW2015/VASP	0.6	0.4	0.4	0.4	0.6	1.0	0.8	0.3
USPP	GBRV14/CASTEP	1.1	1.1	1.1	1.0	1.0	1.4	1.3	1.0
	GBRV14/QE	1.1	1.0	1.0	0.9	1.0	1.4	1.3	1.0
	OTFG9/CASTEP	0.7	0.4	0.5	0.5	0.7	1.0	1.0	0.5
	SSSP/QE	0.5	0.4	0.3	0.3	0.5	0.9	0.8	0.3
	Vdb2/DACAPO	6.3	6.3	6.3	6.3	6.3	6.4	6.5	6.2
NCPP	FHI98pp/ABINIT	13.3	13.5	13.4	13.4	13.2	13.0	13.2	13.4
	HGH/ABINIT	2.2	2.2	2.2	2.2	2.0	2.3	2.2	2.1
	HGH-NLCC/BigDFT	1.1	1.1	1.1	1.1	1.0	1.2	1.1	1.0
	MBK2013/OpenMX	2.0	2.1	2.1	2.1	1.9	1.8	1.8	2.0
	ONCVPSP(PD0.1)/ABINIT	0.7	0.7	0.7	0.7	0.6	1.0	0.8	0.6
	ONCVPSP(SG15)1/QE	1.4	1.4	1.3	1.3	1.3	1.6	1.5	1.3
	ONCVPSP(SG15)2/CASTEP	1.4	1.4	1.4	1.4	1.3	1.6	1.5	1.4

All calculations done with the PBE functional:
This is VERIFICATION (the codes are solving the equations correctly),
NOT VALIDATION (the results are realistic).

LDA and Ceperly-Alder

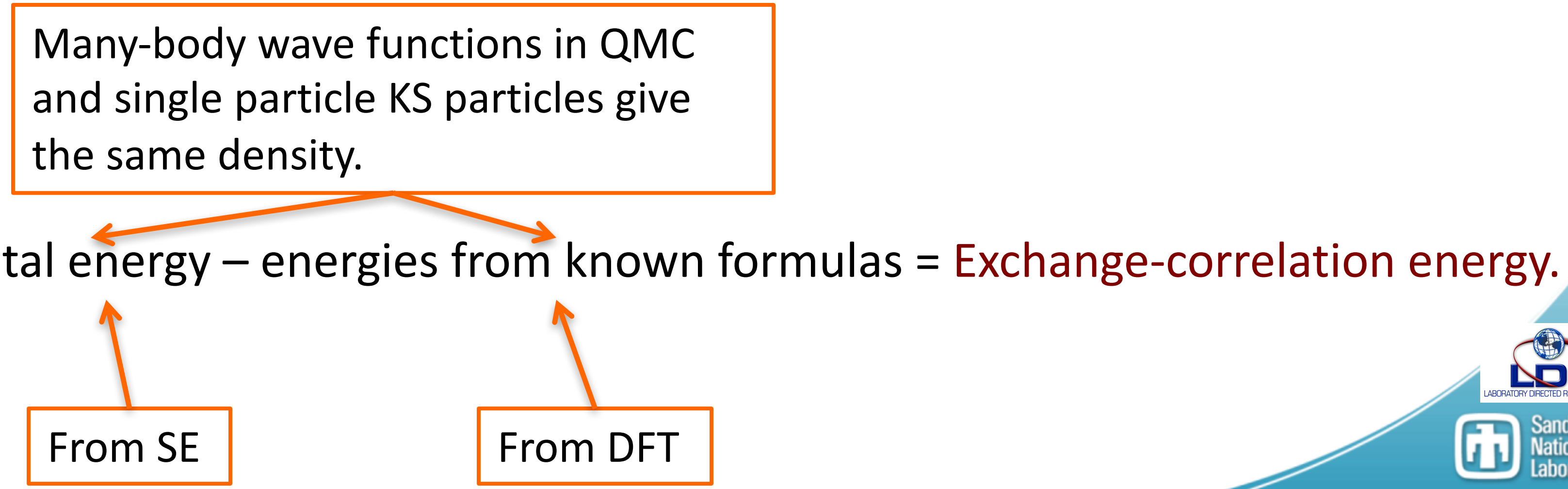
Ceperly and Alder, PRL 45, 566 (1980).

Quantum Monte Carlo calculations of the ground-state energy of uniform electron gases (model systems) of different densities.

Most correlation functionals in use today are based on their data.

ALL LDA correlation functionals in common use are based on (fitted to) their data.

(Before 1980, for example, Wigner correlation was used)



Many-body wave functions in QMC and single particle KS particles give the same density.

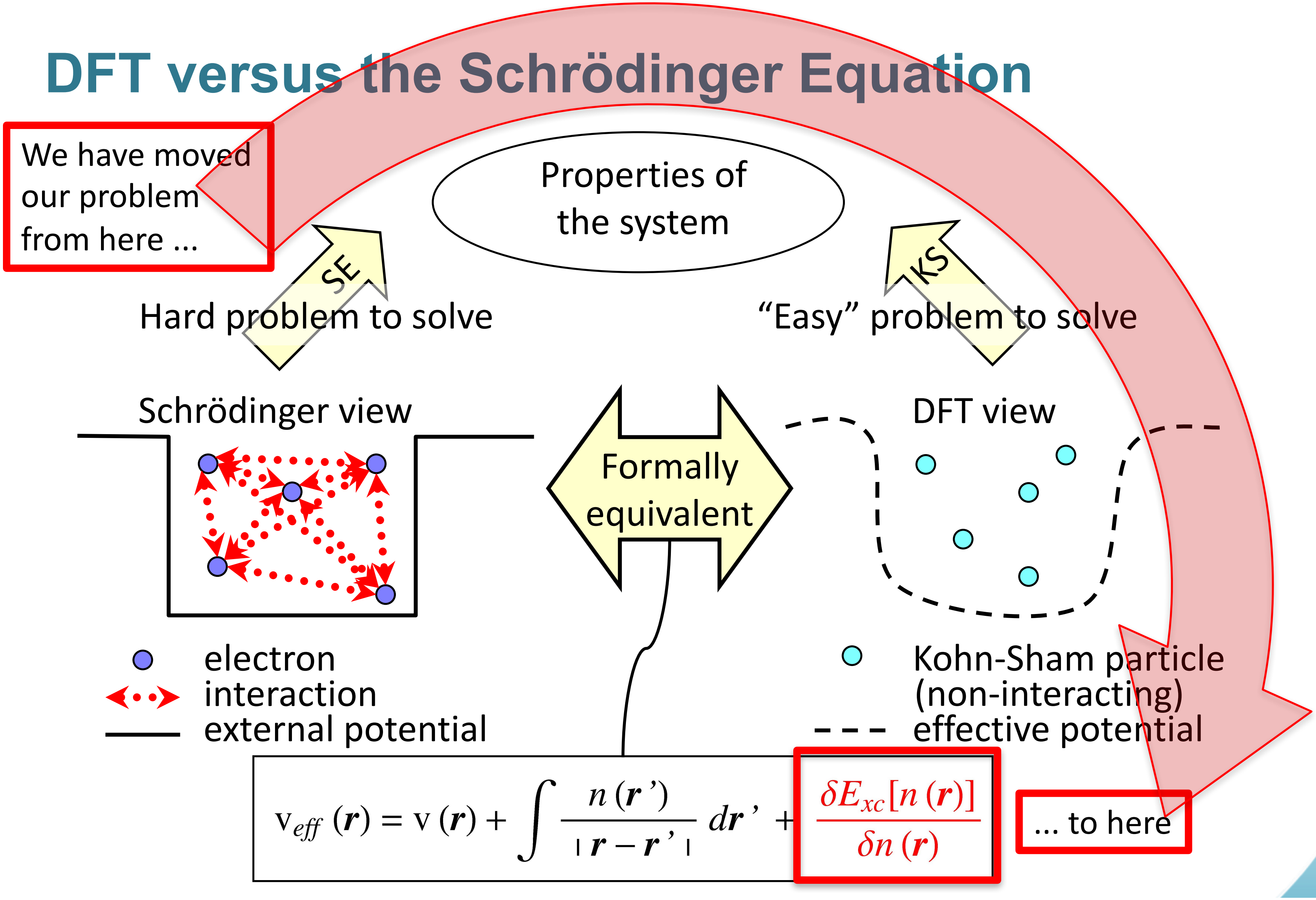
Total energy – energies from known formulas = Exchange-correlation energy.

From SE

From DFT

DFT versus the Schrödinger Equation

Ann E. Mattsson



We have moved our problem from here ...

Properties of the system

SE

KS

Hard problem to solve

"Easy" problem to solve

Schrödinger view

Formally equivalent

DFT view

● electron

◀··▶ interaction

— external potential

○ Kohn-Sham particle (non-interacting)

- - - effective potential

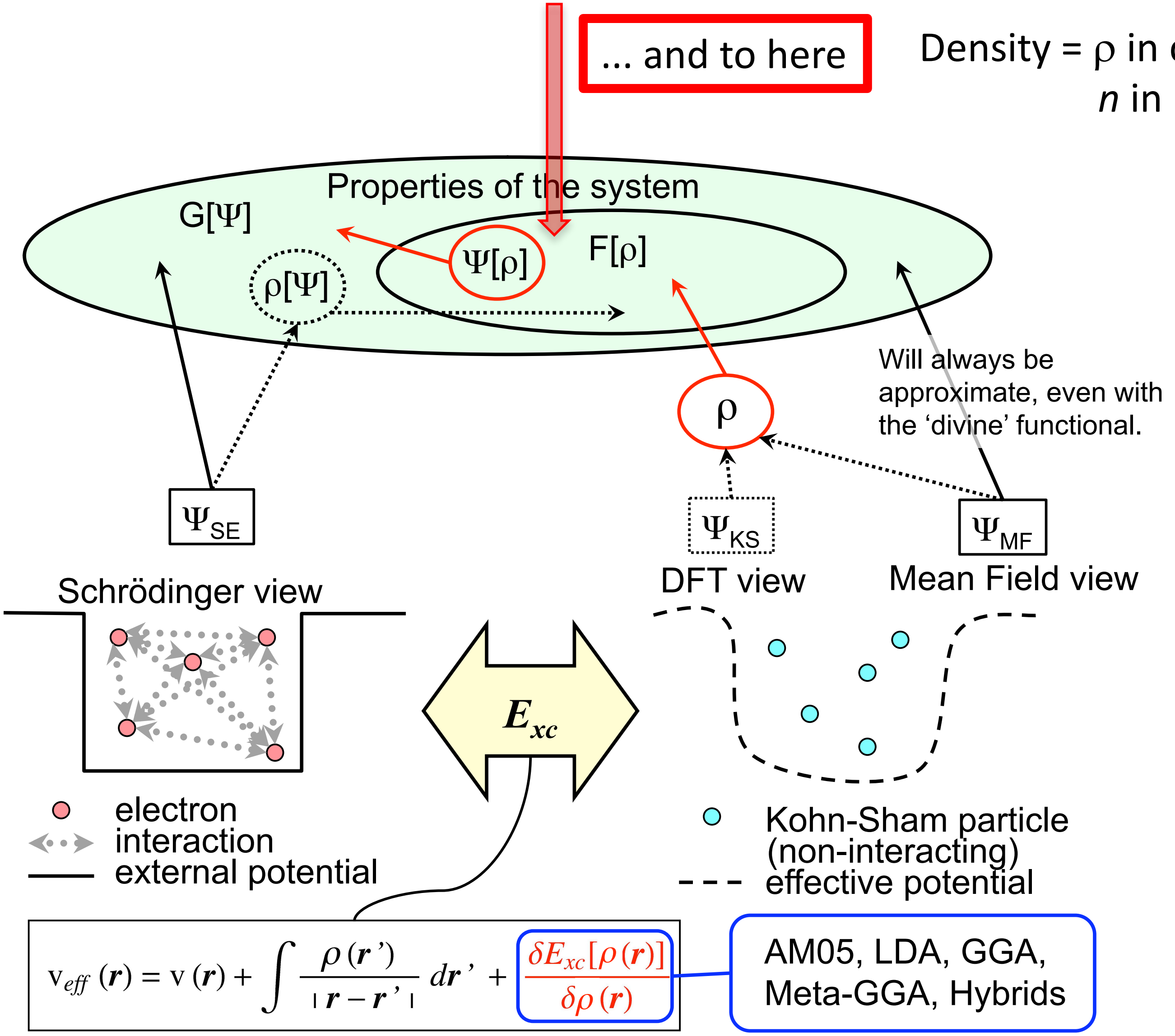
$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + \boxed{\frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}}$$

... to here

All many-body effects are included in the effective potential via the Exchange-Correlation functional, $E_{xc}[n(\mathbf{r})]$.

DFT versus Mean Field Theory

Density = ρ in chemistry
n in physics



Will always be approximate, even with the 'divine' functional.

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + \boxed{\frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}}$$

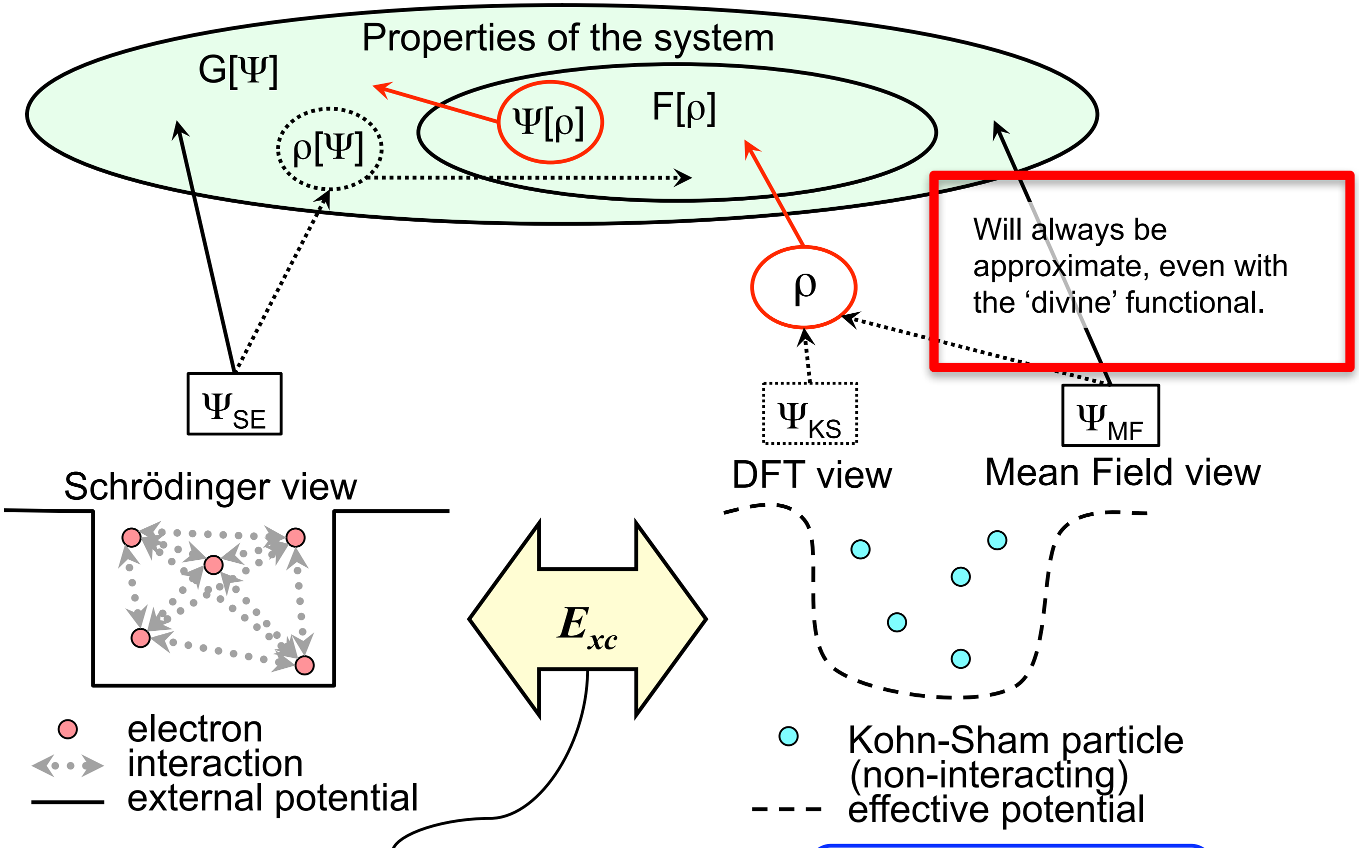
AM05, LDA, GGA, Meta-GGA, Hybrids

From "Metallic Systems: A Quantum Chemist's Perspective", the chapter "Some practical considerations for density functional theory studies of chemistry at metal surfaces" published by Taylor and Francis in 2011.

DFT versus Mean Field Theory

Ann E. Mattsson

Density = ρ in chemistry
n in physics



Will always be approximate, even with the 'divine' functional.

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}$$

AM05, LDA, GGA, Meta-GGA, Hybrids

From "Metallic Systems: A Quantum Chemist's Perspective", the chapter "Some practical considerations for density functional theory studies of chemistry at metal surfaces" published by Taylor and Francis in 2011.

Copenhagen interpretation of Quantum Mechanics (quotes from Wikipedia)

Bohr emphasized that science is concerned with predictions of the outcomes of experiments, and that any additional propositions offered are not scientific but meta-physical

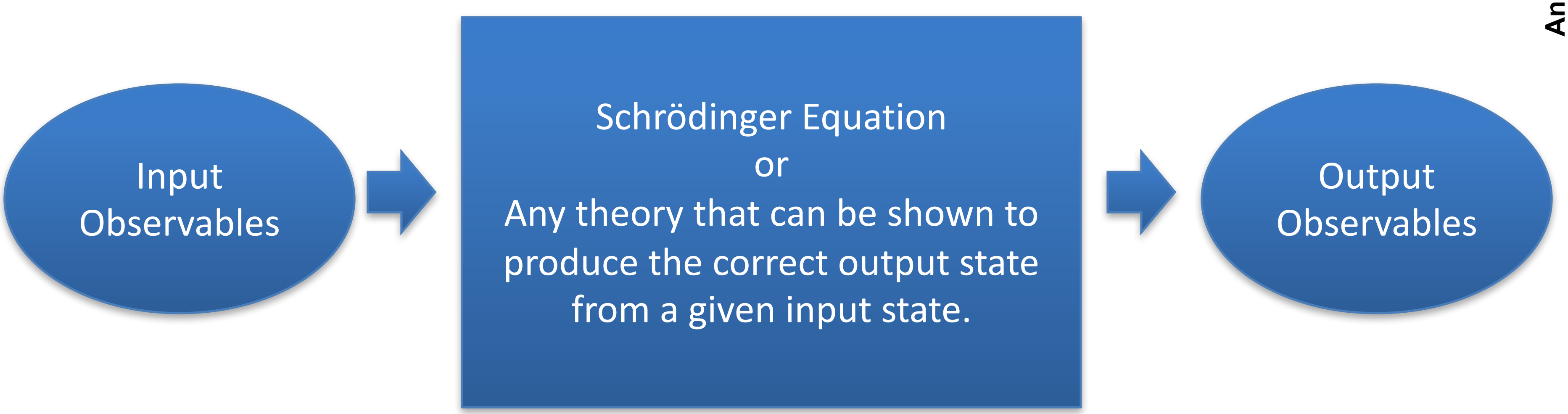
The Copenhagen Interpretation denies that the wave function is anything more than a theoretical concept

… the wave function is merely a mathematical tool for calculating the probabilities in a specific experiment

Carl Friedrich von Weizsäcker suggested instead that the Copenhagen interpretation follows the principle "What is observed certainly exists; about what is not observed we are still free to make suitable assumptions

Generalization

Ann E. Mattsson



Input Observables

Schrödinger Equation
or
Any theory that can be shown to produce the correct output state from a given input state.

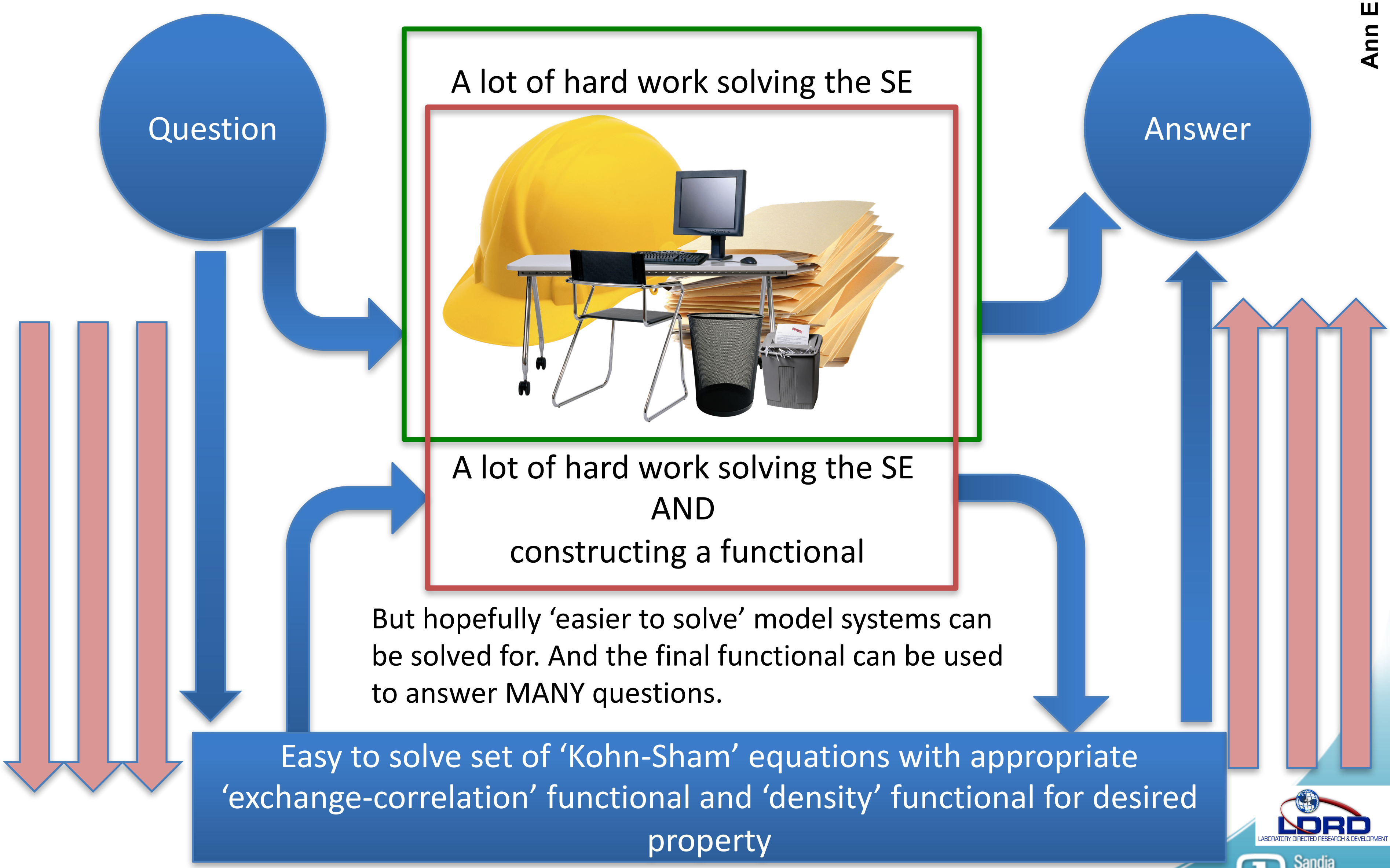
Output Observables

We always trade a hard-to-solve many-body wave-function equation for an easier-to-solve set of ‘Kohn-Sham’ equations.

But this is only a winning situation if a good approximation for the ‘exchange-correlation’ functional can be found and a ‘density’ functional giving the observable is available or can be constructed.

Functionals vs. direct solve of SE

Ann E. Mattsson



Question

A lot of hard work solving the SE

Answer

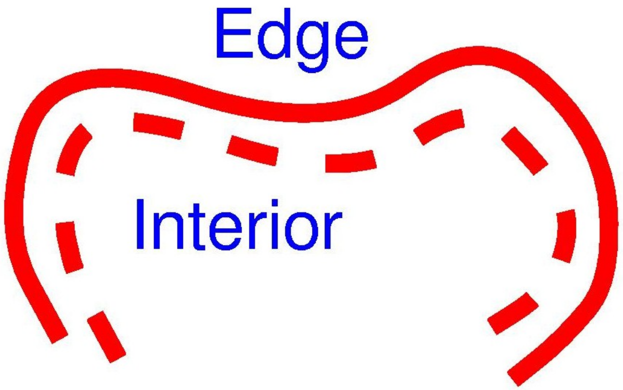
A lot of hard work solving the SE
AND
constructing a functional

But hopefully 'easier to solve' model systems can be solved for. And the final functional can be used to answer MANY questions.

Easy to solve set of 'Kohn-Sham' equations with appropriate 'exchange-correlation' functional and 'density' functional for desired property

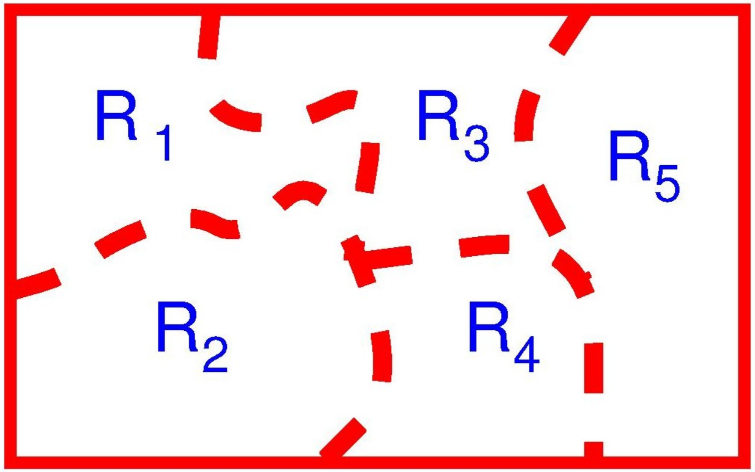
Subsystem functionals

Original Kohn and Mattsson approach



Kohn, Mattsson PRL 81, 3487 (1998)

Generalized Idea



Every subsystem functional is designed to capture, via a model system, a specific type of physics, appropriate for a particular subsystem.

Ann E. Mattsson

Subsystem functionals

Constructing a general purpose functionals
from specialized functionals

$$E_{xc} = \int_V n(\mathbf{r})\, \epsilon_{xc}(\mathbf{r};[n])\, dV$$

Use specialized functionals in the different subsystems

Divide integration over V into integrations over subsystems

Note: The integration over subsystems is done automatically by the use of an interpolation function

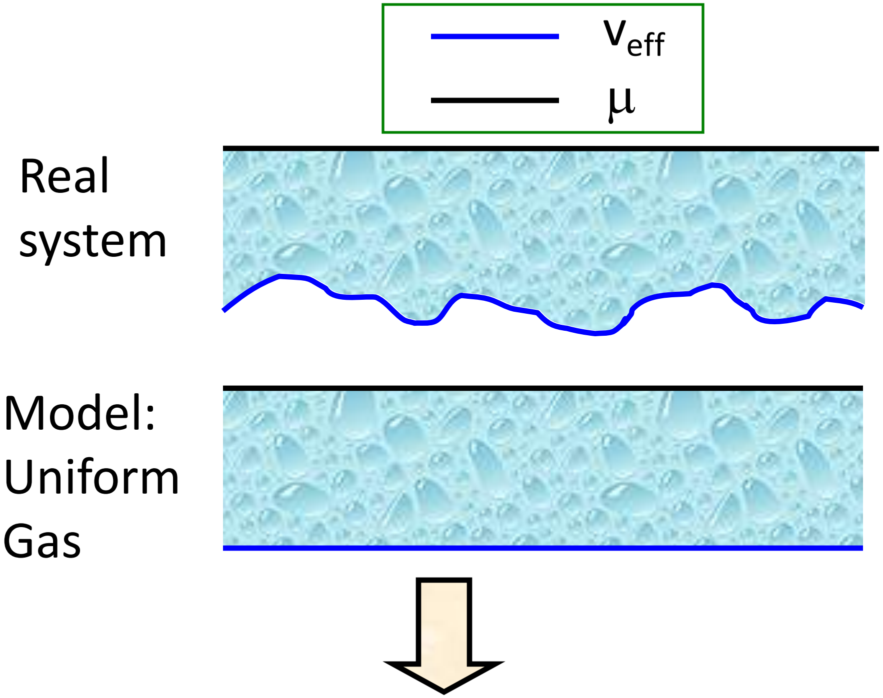
For the subsystem functional scheme we need:

1) One specialized functional for each subsystem we want to describe.

2) An interpolation index that can tell us the character of the system in each point so that we can apply the different specialized functionals accordingly.

A specialized functional: The LDA functional

Ann E. Mattsson



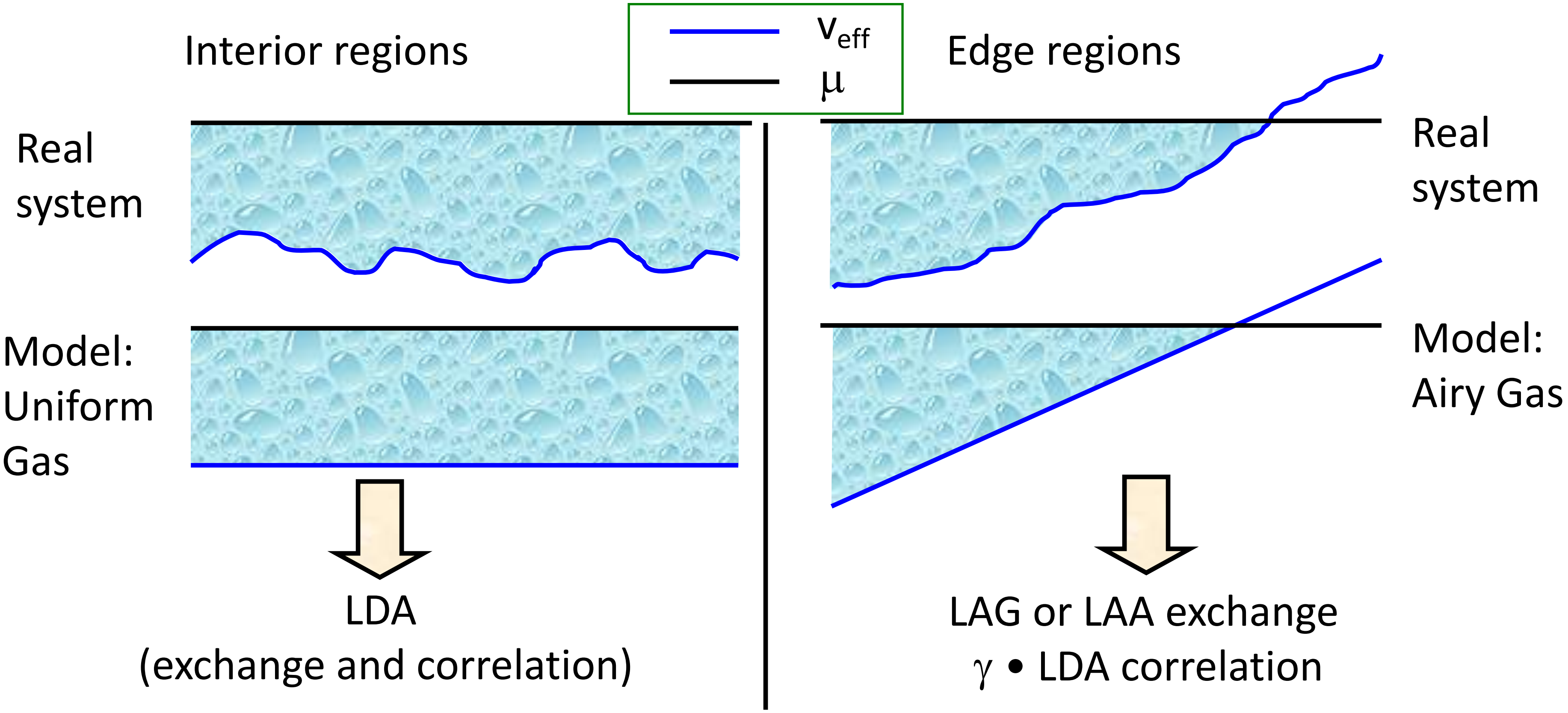
LDA
(exchange and correlation)

Assume each point in the real system contribute the amount of exchange-correlation energy as would a uniform electron gas with the same density.

Obviously exact for the uniform electron gas.

Basic concept and first explicit LDA published in 1965 (Kohn and Sham).

A general functional from specialized functionals: AM05, PRB 72, 085108 (2005)



Interior regions

Real system

Model: Uniform Gas

LDA
(exchange and correlation)

Edge regions

Real system

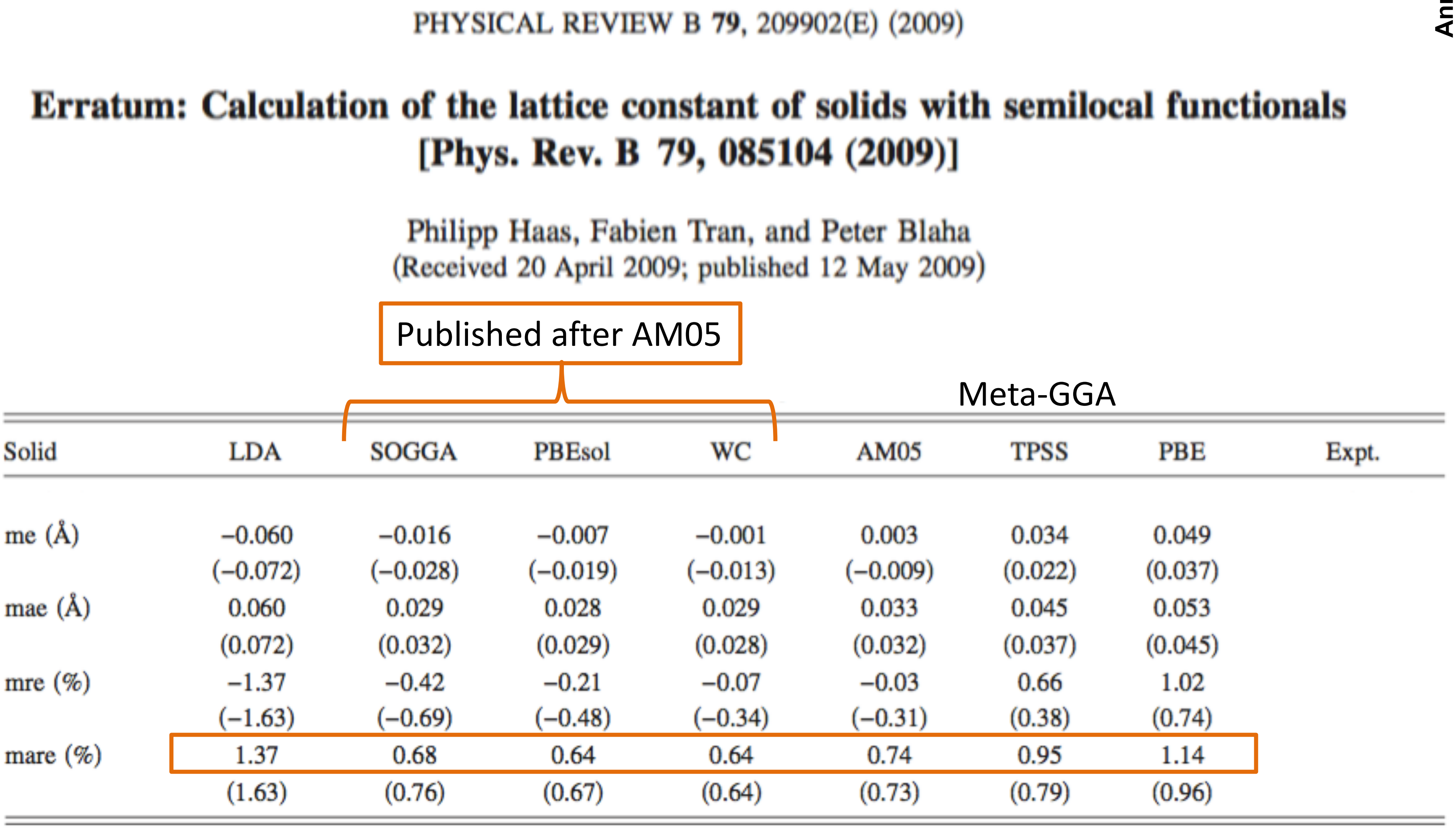
Model: Airy Gas

LAG or LAA exchange
γ • LDA correlation

Interpolation
with an index based on the gradient of the density

Two constants (one is γ above, one is in interpolation index)
are determined by fitting to yield correct jellium surface energies.

Performance of AM05: Test on 60 solids



PHYSICAL REVIEW B **79**, 209902(E) (2009)

Erratum: Calculation of the lattice constant of solids with semilocal functionals [Phys. Rev. B 79, 085104 (2009)]

Philipp Haas, Fabien Tran, and Peter Blaha
(Received 20 April 2009; published 12 May 2009)

Published after AM05

Meta-GGA

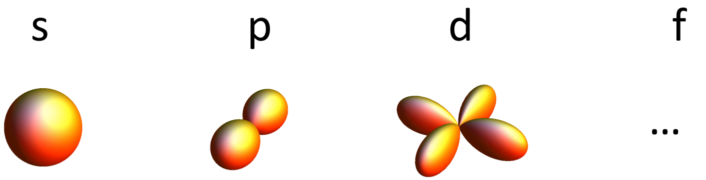
Solid	LDA	SOGGA	PBEsol	WC	AM05	TPSS	PBE	Expt.
me (Å)	−0.060	−0.016	−0.007	−0.001	0.003	0.034	0.049	
	(−0.072)	(−0.028)	(−0.019)	(−0.013)	(−0.009)	(0.022)	(0.037)	
mae (Å)	0.060	0.029	0.028	0.029	0.033	0.045	0.053	
	(0.072)	(0.032)	(0.029)	(0.028)	(0.032)	(0.037)	(0.045)	
mre (%)	−1.37	−0.42	−0.21	−0.07	−0.03	0.66	1.02	
	(−1.63)	(−0.69)	(−0.48)	(−0.34)	(−0.31)	(0.38)	(0.74)	
mare (%)	1.37	0.68	0.64	0.64	0.74	0.95	1.14	
	(1.63)	(0.76)	(0.67)	(0.64)	(0.73)	(0.79)	(0.96)	

Available before AM05

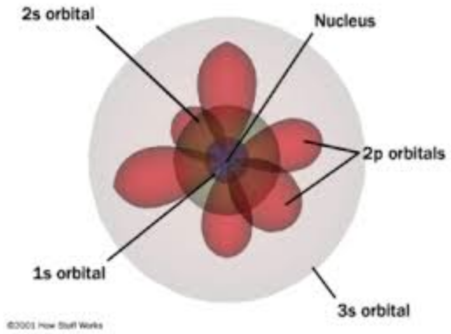
“Strongly correlated” systems

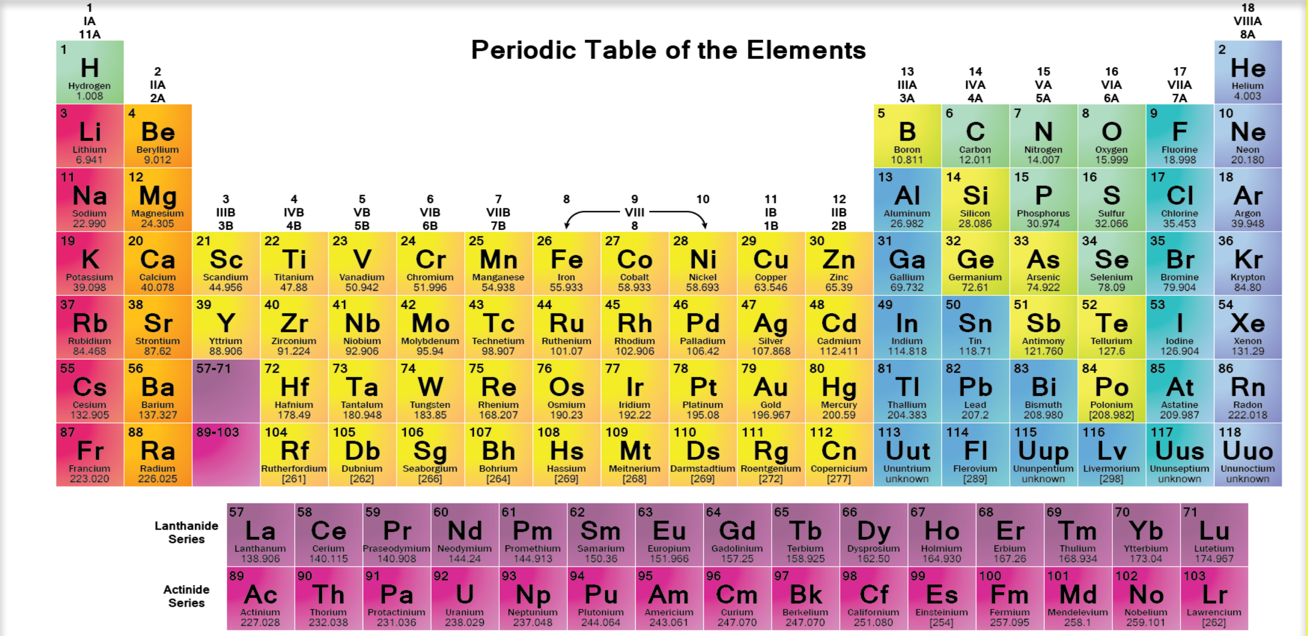
Ann E. Mattsson

DFT/AM05 works well for most materials, in particular those containing only s-, p-, and sp- elements.



Additional electrons behave more complicated the further down in the periodic table we go.





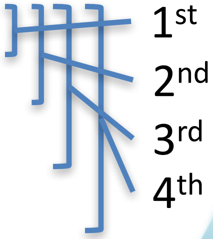
Periodic Table of the Elements

1 IA 11A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.09	35 Br Bromine 79.904	36 Kr Krypton 84.80
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Lanthanide Series	57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Alkali Metal	Alkaline Earth	Transition Metal	Semimetal	Nonmetal	Basic Metal	Halogen	Noble Gas	Lanthanide	Actinide
s	sp	d	sp	sp	sp	p	-	f	f

Type of electrons governing properties

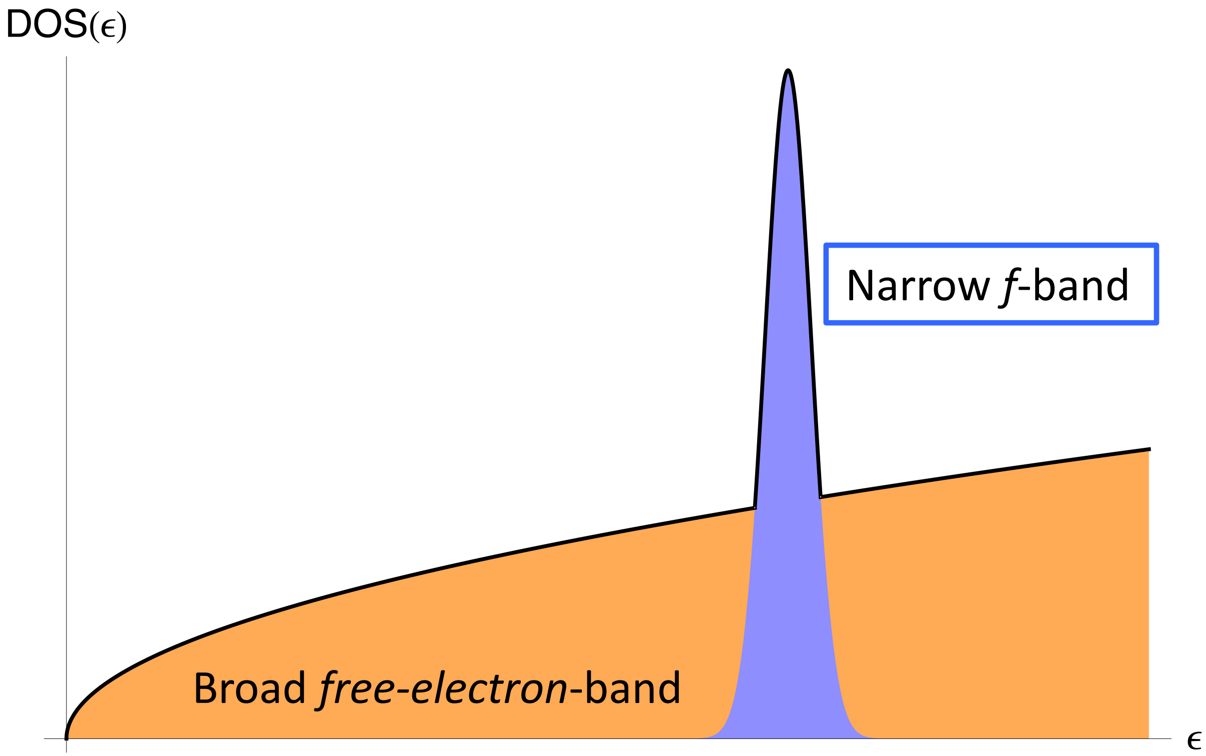


1x2 s-electrons	1st
3x2 p-electrons	2nd
5x2 d-electrons	3rd
7x2 f-electrons	4th

Gets complicated very fast beyond second shell.

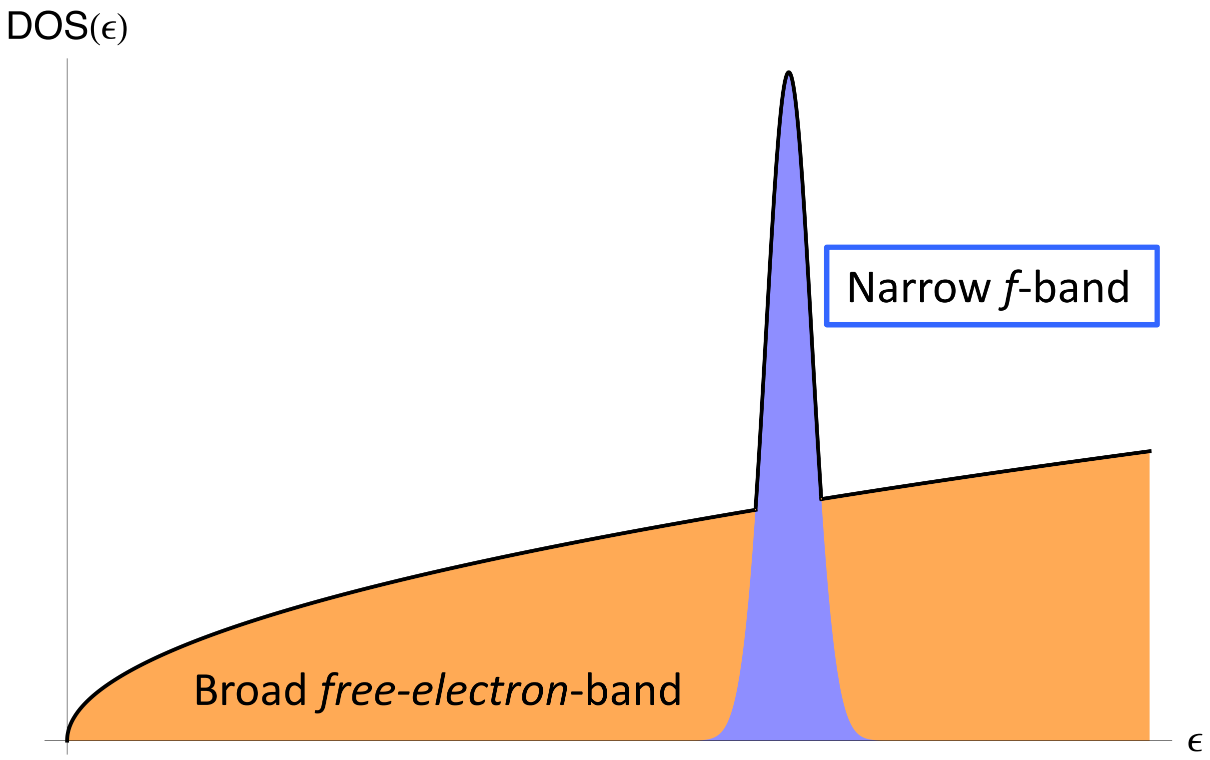
f-electron Physics: Competition between localization and delocalization

Ann E. Mattsson



The delocalized electrons in the broad *free-electron* band and the localized electrons in the narrow *f*-electron band are behaving very differently. The interesting physics and chemistry of *f*-electron materials are governed by a competition between these two different pictures.

f-electron Physics: Density Functional Theory



LDA and other functionals based on the uniform electron gas can be expected to work on the broad free-electron band.

The Pauli exclusion principle embedded in the exchange energy is the main source for describing the fermionic nature of electrons. Hybrids and exact exchange are considered needed for discrete levels.

Since the physics of *f*-electron materials is due to the competition between these two types of states, a functional needs to be able to describe the two situations equally well.

Functionals are applied in real space. How do we take the discrete level/uniform electron gas picture to real space?.

Subsystem functionals

Ann E. Mattsson

Constructing a general purpose functionals
from specialized functionals

$$E_{xc} = \int_V n(\mathbf{r})\, \epsilon_{xc}(\mathbf{r};[n])\, dV$$

Use specialized functionals in the different subsystems

Divide integration over V into integrations over subsystems

Note: The integration over subsystems is done automatically by the use of an interpolation function

For the subsystem functional scheme we need:

1) One specialized functional for each subsystem we want to describe.

2) An interpolation index that can tell us the character of the system in each point so that we can apply the different specialized functionals accordingly.

Subsystem Functional Scheme:

$$E_{xc} = \int_V n(\vec{r})\ \varepsilon_{xc}(\vec{r};[n])\ dV$$

Dividing V into sub-regions where different subsystem functionals apply: Interpolation index.

Specialized functionals in different subsystems

?

Interpolation Index:

?

Interior physics:

Uniform electron gas

Surface physics:

Airy Gas

Electron localization function (ELF)

A.D. Becke and K. E. Edgecombe, J. Chem. Phys. **92**, 5397 (1990)

Interpretation in terms of fermion character: B. Silvi and A. Savin, Nature **371**, 683 (1994)
Note: Kohn-Sham particles are fermions! Despite the name, not only valid for electrons.

$$ELF = \frac{1}{1+(D/D_h)^2}$$

$$D = \tau - \frac{1}{8}\frac{|\nabla n|^2}{n}$$

$$D_h = \frac{3}{10}(3\pi^2)^{2/3} n^{5/3}$$

τ: kinetic energy density
n: electron density

D: kinetic energy excess with respect to a boson gas.
D_h: kinetic energy of a uniform electron gas.

$D/D_h = \alpha_{\mathrm{Perdew}}$

D = 0: kinetic energy is equivalent to that in a boson gas *with the same density*. Fermions do not need to adjust their kinetic energy because of other fermions nearby.

D = D_h: Uniform electron gas by construction. All fermions have same potential energy and need to adjust their kinetic energy to stay different.

D -> ∞: Very high kinetic energy needed for fermions in classically forbidden region.

ELF ≈ 1: strong localization, discrete levels.
ELF ≈ 1/2: uniform electron gas like
ELF ≈ 0: Classically forbidden region.

Ann E. Mattsson

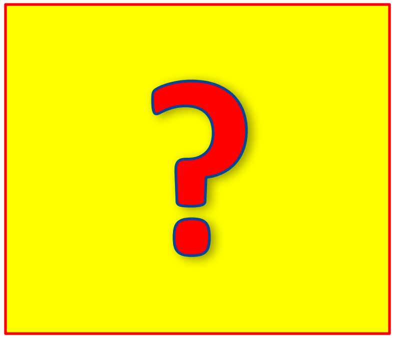
Subsystem Functional Scheme:

Ann E. Mattsson

$$E_{xc} = \int_V n(\vec{r})\ \varepsilon_{xc}(\vec{r};[n])\ dV$$

Dividing V into sub-regions where different subsystem functionals apply: Interpolation index.

Specialized functionals in different subsystems



ELF ≈ 1

(α_{Perdew}=0, atom)

(α_{Perdew}=1)

ELF ≈ 1/2

Interpolation Index: **ELF**

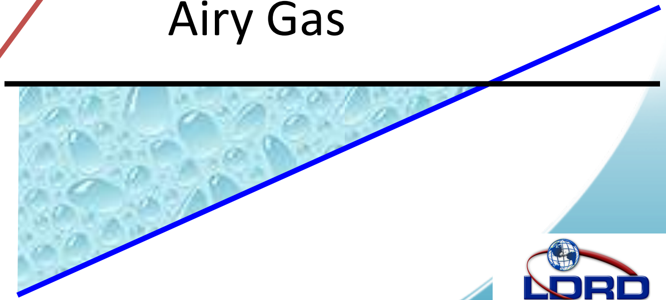
ELF ≈ 0

Interior physics:

Uniform electron gas

Surface physics:

Airy Gas



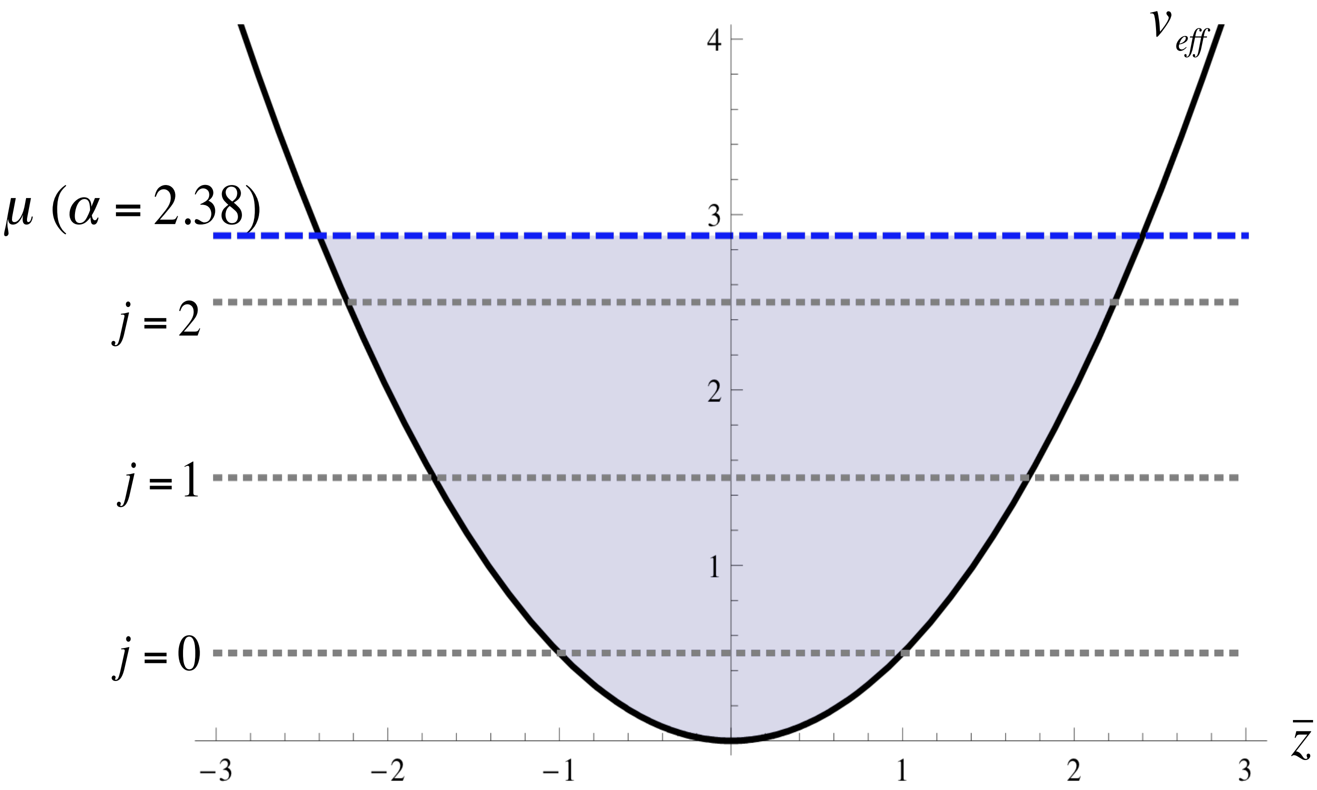
(α_{Perdew}-> ∞, jellium surface)

Important to use same definition of exchange in each subsystem: We use conventional exchange.
Armiento and Mattsson, PRB **66**, 165117 (2002).

Harmonic Oscillator model (HO)

Hao, Armiento and Mattsson Phys, Rev. B **82**, 115103 (2010).

HO model: Localized electron levels in a continuum.



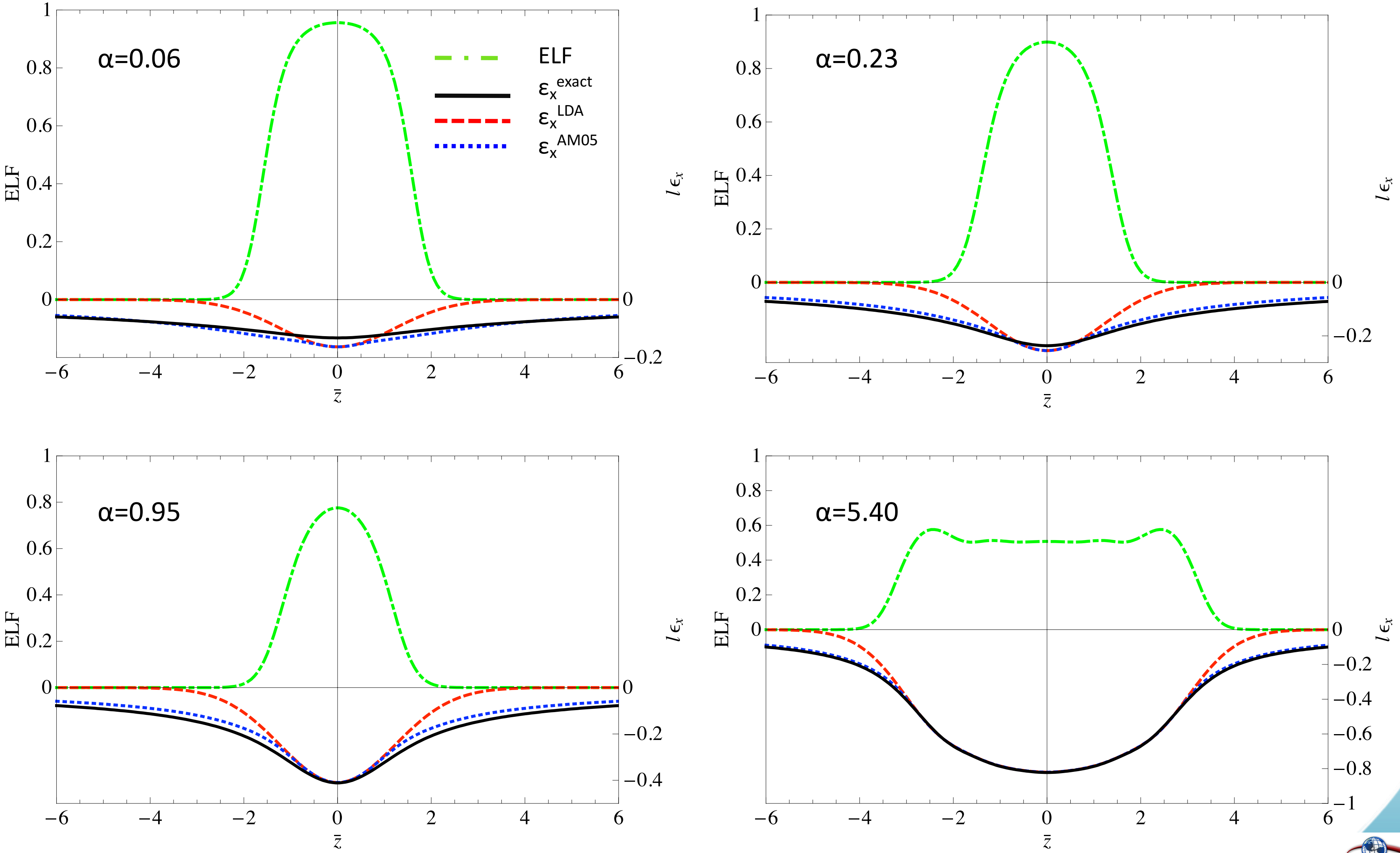
Energy of subbands $\varepsilon_j = (j + \frac{1}{2})\frac{1}{l^2}$

Chemical potential $\mu = (\alpha + \frac{1}{2})\frac{1}{l^2}$

α characterizes how many subbands have been occupied, and determines the level of confinement.

ELF in HO systems versus Exchange Energy

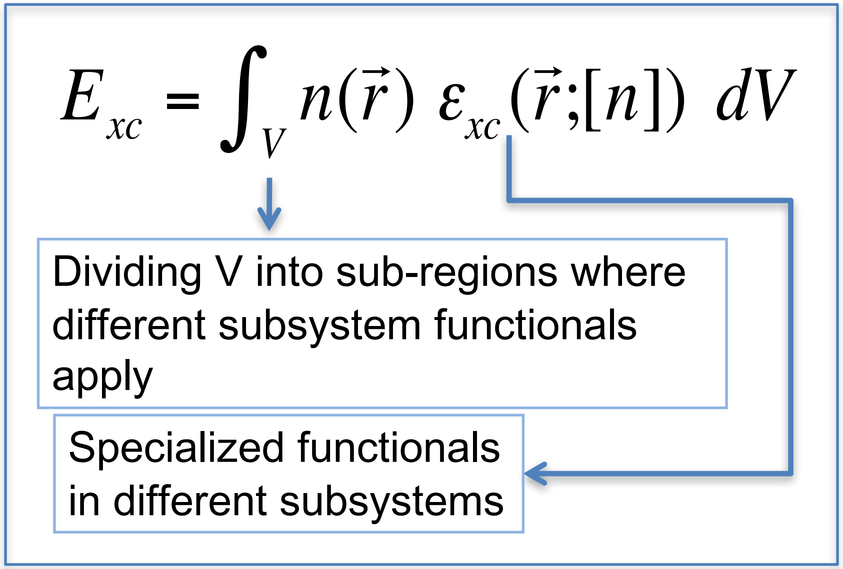
Ann E. Mattsson



ELF is correlated with the exchange energy errors!

Subsystem Functional Scheme:

Ann E. Mattsson

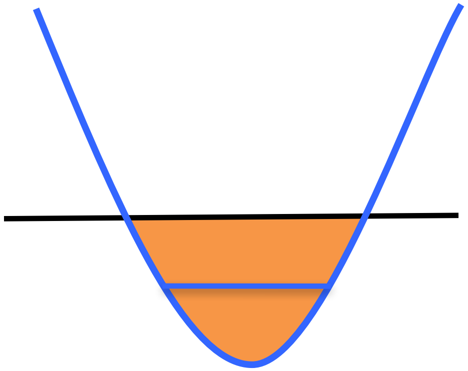


$$E_{xc} = \int_V n(\vec{r})\ \varepsilon_{xc}(\vec{r};[n])\ dV$$

Dividing V into sub-regions where different subsystem functionals apply

Specialized functionals in different subsystems

Confinement physics:
Harmonic oscillator gas



Interpolation
Index:
ELF

Interior physics:
Uniform electron gas

Surface physics:
Airy Gas

Feng Hao, Rickard Armiento, and Ann E. Mattsson
Journal of Chemical Physics **140**, 18A536 (2014).

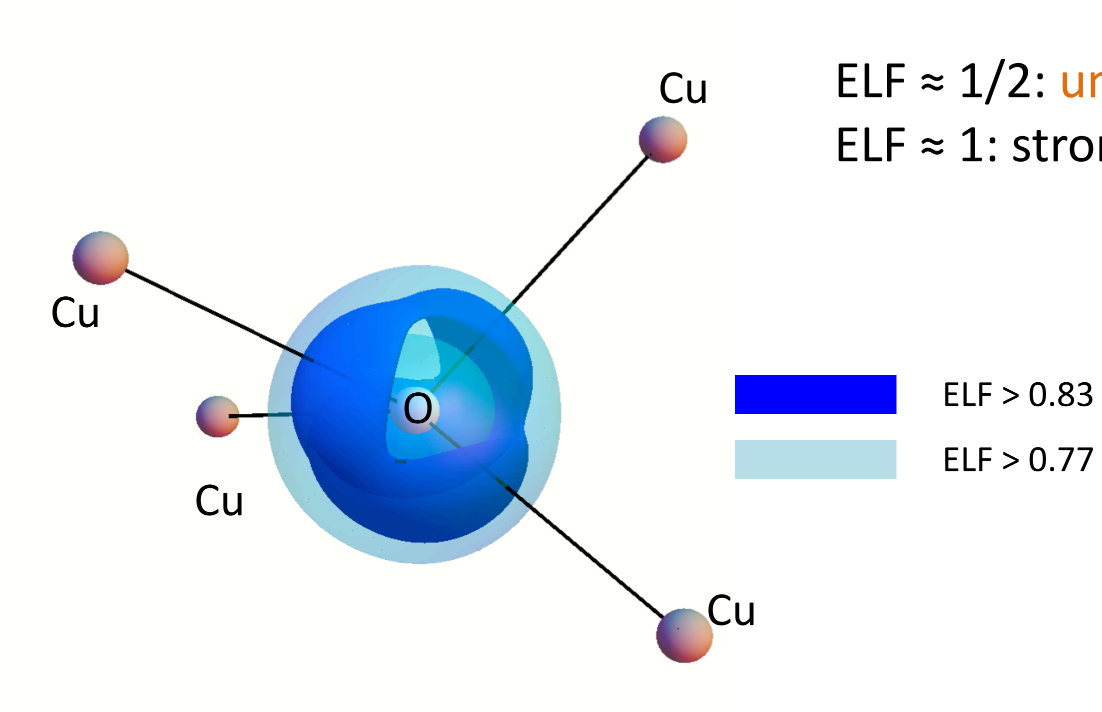
Summary

Tutorial Review: Density functional theory for *d*- and *f*-electron materials and compounds, Ann E. Mattsson and John M. Wills, International Journal of Quantum Chemistry **116**, 834 (2016).

- For a large class of materials, from Iron and up, we might need to develop and use the Dirac Equation based KS equations.
- The interesting properties of *f*-electron systems comes from a simultaneous existence of free and discrete level electrons.
- The challenge we have is to describe free electrons and discrete level electrons equally well in a unified picture.
- The ELF index can be used to find regions in real space where discrete level physics needs to be taken into account.
- We have identified the HO gas as a model system that can be used to gain insight about this kind of physics.
- We will use the HO gas model system for creating a functional suitable for these systems via the subsystem functional scheme.

ELF in a ‘real’ system: CuO, transition metal oxide

ELF ≈ 1/2: uniform electron gas like
ELF ≈ 1: strong localization, discrete levels



CuO: Monoclinic structure obtained when starting from the experimental structure with each dimension scaled by 3%

Feng Hao, Rickard Armiento, and Ann E. Mattsson
Journal of Chemical Physics **140**, 18A536 (2014).

The high ELF regions are around the oxygen atoms. We identify these as the regions where <u>hybridization</u> in solid materials occur.

Quantum Mechanics

Dirac (1929)

> “ The general theory of quantum mechanics is now almost complete… The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. ”

P.A.M. Dirac, Proc. R. Soc. London Ser. A 123, 714 (1929).

However, the Schrödinger equation is the non-relativistic limit of the Dirac equation. In many materials, at least from Iron and up, relativistic effects, and the associated spin-orbit coupling, can be dominating the physics.

We need to base DFT on the relativistic Dirac Equation

Relativistic Kohn-Sham equations: Functionals

$$\left(c\,\boldsymbol{\alpha}\cdot\left(\boldsymbol{p}-\boxed{\frac{e\boldsymbol{A}_{\mathit{eff}}}{c}}\right)+\begin{pmatrix}I&0\\0&I\end{pmatrix}V_{\mathit{eff}}(\boldsymbol{r})+\beta\,mc^2\right)\psi_n(\boldsymbol{r})=E_n\,\psi_n(\boldsymbol{r})$$

$$\begin{aligned}V_{\mathit{eff}}(\boldsymbol{r})&=-e\left(A^0_{ext}(\boldsymbol{r})+\int d^3r'\,\frac{J^0(\boldsymbol{r'})}{|\boldsymbol{r}-\boldsymbol{r'}|}+\frac{\delta E_{xc}[J^\mu]}{\delta J^0(\boldsymbol{r})}\right)\\ \boxed{e\boldsymbol{A}_{\mathit{eff}}(\boldsymbol{r})}&=-e\left(\boldsymbol{A}_{ext}(\boldsymbol{r})+\int d^3r'\,\frac{\boldsymbol{J}(\boldsymbol{r'})}{|\boldsymbol{r}-\boldsymbol{r'}|}+\frac{\delta E_{xc}[J^\mu]}{\delta \boldsymbol{J}(\boldsymbol{r})}\right)\end{aligned}$$

$$J^\mu=(J^0,\boldsymbol{J})=-e\sum_{-mc^2<E_n<E_F}\left(\psi_n^\dagger\psi_n,\boxed{\psi_n^\dagger\boldsymbol{\alpha}\,\psi_n}\right)$$

But functionals available from non-relativistic Kohn-Sham theory use spin densities, not currents. The vector potential term is the tricky one, coupling upper and lower components.

From currents to spin densities

Ann E. Mattsson

Spin density:

$$\boldsymbol{S} = -\sum_{-mc^2<E_n<E_F} \psi_n^\dagger \, \beta \, \boldsymbol{\Sigma} \, \psi_n \qquad \Sigma_k = \begin{pmatrix} \sigma_k & 0 \\ 0 & \sigma_k \end{pmatrix}$$

Gordon decomposition

$$\boldsymbol{J} = \boldsymbol{I} + \mu_B \nabla \times \boldsymbol{S}$$

$$\boldsymbol{I} = \frac{e}{2mc} \sum_{-mc^2<E_n<E_F} \left\{ \psi_n^\dagger \, \beta \left[\left(\boldsymbol{p} - \frac{e\boldsymbol{A}_{\mathrm{eff}}}{c} \right) \psi_n \right] + \left[\left(\boldsymbol{p} - \frac{e\boldsymbol{A}_{\mathrm{eff}}}{c} \right) \psi_n \right]^\dagger \beta \, \psi_n \right\}$$

Orbital current: Neglecting this gives…

Approximate Dirac for spin density functionals

Ann E. Mattsson

$$\left(c\,\boldsymbol{\alpha}\cdot\boldsymbol{p} + \mu_B\,\beta\,\boldsymbol{\Sigma}\cdot\boldsymbol{B}_{\mathit{eff}} + \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix} V_{\mathit{eff}}(\boldsymbol{r}) + \beta\,mc^2 \right) \psi_n(\boldsymbol{r}) = E_n\,\psi_n(\boldsymbol{r})$$

$$\begin{aligned} V_{\mathit{eff}}(\boldsymbol{r}) &= -e\left(A^0_{ext}(\boldsymbol{r}) + \int d^3r'\,\frac{J^0(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta E_{xc}[J^\mu]}{\delta J^0(\boldsymbol{r})} \right) \\ \mu_B \boldsymbol{B}_{\mathit{eff}}(\boldsymbol{r}) &= \left(\mu_B \boldsymbol{B}_{ext}(\boldsymbol{r}) + \int d^3r'\,\frac{\boldsymbol{M}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta E_{xc}[J^0,\boldsymbol{M}]}{\delta \boldsymbol{M}(\boldsymbol{r})} \right) \end{aligned}$$

$$\boldsymbol{M} = \mu_B \boldsymbol{S}$$

Now ordinary DFT spin functionals can be used.

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Sandia National Laboratories

Summary Thorium

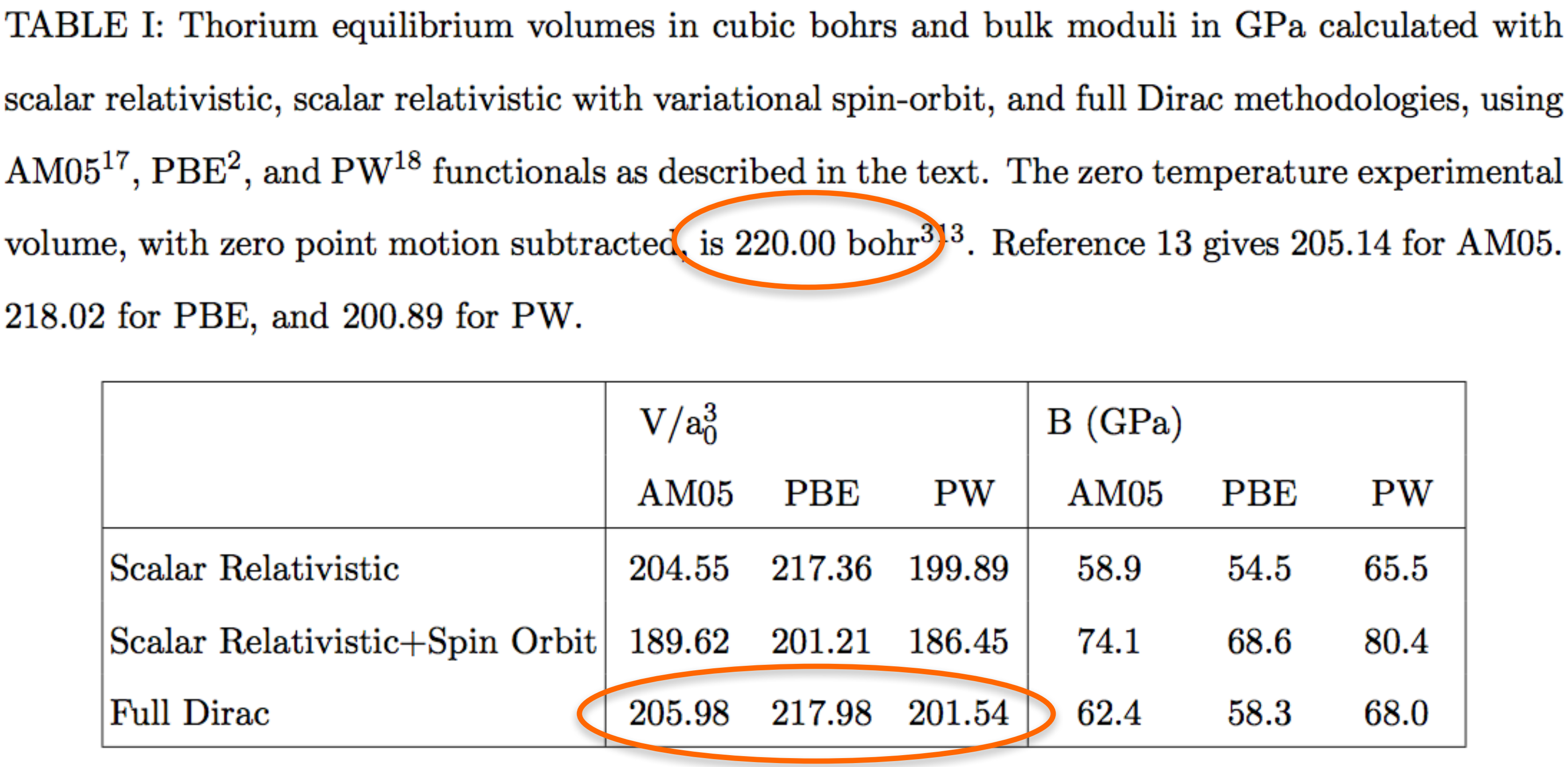


TABLE I: Thorium equilibrium volumes in cubic bohrs and bulk moduli in GPa calculated with scalar relativistic, scalar relativistic with variational spin-orbit, and full Dirac methodologies, using AM05[17], PBE[2], and PW[18] functionals as described in the text. The zero temperature experimental volume, with zero point motion subtracted, is 220.00 bohr^3[13]. Reference 13 gives 205.14 for AM05. 218.02 for PBE, and 200.89 for PW.

	V/a_0^3			B (GPa)		
	AM05	PBE	PW	AM05	PBE	PW
Scalar Relativistic	204.55	217.36	199.89	58.9	54.5	65.5
Scalar Relativistic+Spin Orbit	189.62	201.21	186.45	74.1	68.6	80.4
Full Dirac	205.98	217.98	201.54	62.4	58.3	68.0

Note: PBE is giving 7% too large volume for gold. Generally underbinding.
"When PBE gets the right equilibrium volume, you should get suspicious".
Seen like an indication that a hybrid functional or exact exchange is needed.
Confinement physics…

Ann E. Mattsson

Thank you for your attention

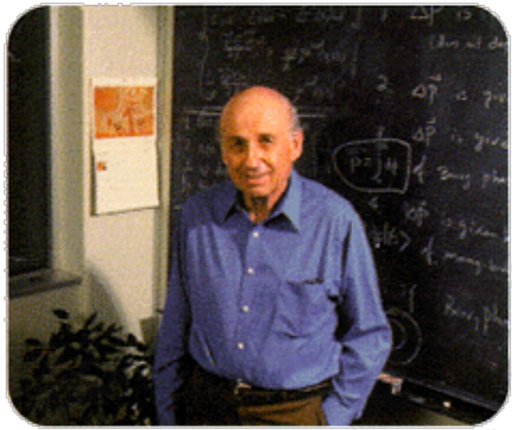


photo: Dave Folks

Walter Kohn

University of California
at Santa Barbara, USA

This is the photo on the Nobel Poster that I still prominently display in my office. I am standing at the blackboard just out of view.

Walter Kohn was presented receiving an honorary Doctor of Science degree by the Harvard University (AP Photo/Steven Senne).

Obituary for Walter Kohn (1923-2016)
Karlheinz Schwarz, Lu J. Sham, Ann E. Mattsson and Matthias Scheffler
Computation **4**, 40 (2016).