

PERSPECTIVE ON SCAN AND ITS BAND GAPS

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**SUPPORTED BY THE U.S. DEPARTMENT OF ENERGY, EFRC CCDM
(CENTER FOR THE COMPUTATIONAL DESIGN OF FUNCTIONAL
LAYERED MATERIALS)**

SCAN WORKSHOP, MAY 18, 2017

PERSPECTIVE ON DENSITY FUNCTIONAL APPROXIMATIONS FOR THE EXCHANGE-CORRELATION ENERGY

THE NEGATIVE EXCHANGE-CORRELATION ENERGY IS MAINLY THE LOWERING OF THE ELECTRON-ELECTRON COULOMB REPULSION ENERGY ARISING FROM THE FACT THAT ELECTRONS AVOID ONE ANOTHER DUE TO THE PAULI EXCLUSION PRINCIPLE AND THE COULOMB REPULSION. THIS HAPPENS MORE EFFECTIVELY WHEN ATOMS ARE CLOSER TOGETHER, SO **THE XC ENERGY IS “NATURE’S GLUE”**, ACCOUNTING FOR MOST OF THE BINDING OF ONE ATOM TO ANOTHER TO MAKE A MOLECULE, A COMPLEX, OR A SOLID.

KOHN AND SHAM 1965 PROVED THAT THE EXACT EXCHANGE-CORRELATION ENERGY IS A FUNCTIONAL OF THE ELECTRON DENSITY, AND PROPOSED THE LOCAL DENSITY APPROXIMATION (LDA).

LDA WAS CONSTRUCTED TO SATISFY AN APPROPRIATE NORM: TO BE EXACT FOR AN ELECTRON GAS OF ANY UNIFORM DENSITY.

LDA WORKED MUCH BETTER THAN EXPECTED. IN 1975-76, LANGRETH & PERDEW, AND GUNNARSSON & LUNDQVIST, DERIVED AN EXACT IF UNCOMPUTABLE EXPRESSION FOR THE XC ENERGY AS THE ELECTROSTATIC INTERACTION BETWEEN THE ELECTRON DENSITY AND THE DENSITY OF THE EXCHANGE-CORRELATION HOLE DENSITY SURROUNDING AN ELECTRON. THEY ALSO DERIVED SOME EXACT CONSTRAINTS ON THE XC HOLE DENSITY, AND ARGUED THAT LDA WORKS FOR REAL DENSITIES BECAUSE IT SATISFIES THESE EXACT HOLE CONSTRAINTS.

EARLY GENERALIZED GRADIENT APPROXIMATIONS (GGAs) WERE CONSTRUCTED BY BUILDING IN THE SECOND-ORDER DENSITY GRADIENT EXPANSION OF THE XC HOLE DENSITY, AND THEN RESTORING THE HOLE CONSTRAINTS.

IN THE 1980's, MANY **EXACT CONSTRAINTS ON THE XC ENERGY AS A FUNCTIONAL OF THE DENSITY** WERE DISCOVERED BY LEVY, LIEB,.... THESE CONSTRAINTS INCLUDED DENSITY-SCALING EQUALITIES AND INEQUALITIES, BOUNDS, AND LIMITS. 11 OF THOSE WERE USED TO CONSTRUCT THE PERDEW-BURKE-ERNZERHOF (PBE) 1996 GGA. $11/17=65\%$

LATER META-GGA's ADDED TWO MORE EXACT CONSTRAINTS: RECOVERY OF THE FOURTH-ORDER GRADIENT EXPANSION, AND ZERO CORRELATION ENERGY FOR ANY ONE-ELECTRON DENSITY. THEY ALSO ADDED APPROPRIATE NORMS, E.G., ONE-ELECTRON ATOMS AND ATOMIC IONS.

THE SCAN META-GGA (SUN, RUZSINSZKY AND PERDEW PRL 2015) WAS CONSTRUCTED TO SATISFY ALL 17 EXACT CONSTRAINTS THAT A COMPUTATIONALLY-EFFICIENT SEMILOCAL FUNCTIONAL CAN, PLUS ADDITIONAL APPROPRIATE NORMS (INCLUDING NEUTRAL ATOMS IN THE LIMIT OF LARGE ATOMIC NUMBER). SCAN IS NOT FITTED TO ANY BONDED SYSTEM, SO ALL ITS BONDING PREDICTIONS ARE GENUINE PREDICTIONS.

THE FOUR EXACT CONSTRAINTS SATISFIED BY SCAN BUT NOT BY TPSS ARE: NON-UNIFORM DENSITY SCALING FOR X , TIGHT LOWER BOUND ON THE X ENERGY OF ANY 2-ELECTRON GROUND-STATE, NONUNIFORM DENSITY SCALING FOR C , AND TIGHT LIEB-OXFORD BOUND ON X_C FOR ANY 2-ELECTRON GROUND STATES.

WE CANNOT SAY WHICH EXACT CONSTRAINTS ARE “MORE IMPORTANT”. ALL THE CONSTRAINTS ARE SYNERGISTICALLY AND INEXTRICABLY ENTANGLED IN SCAN.

FUNCTIONALS THAT ARE HEAVILY FITTED TO ENERGY DIFFERENCES FOR MOLECULES ARE INTERPOLATIVE: THEY CAN BE VERY ACCURATE, BUT ONLY FOR SYSTEMS AND PROPERTIES SIMILAR TO THOSE FOR WHICH THEY HAVE BEEN FITTED. FOR EXAMPLE, MANY FUNCTIONALS WITH 40+ FIT PARAMETERS SERIOUSLY WORSEN THE ELECTRON DENSITIES OF ATOMS AND MOLECULES (MEDVEDEV ET AL. SCIENCE 2017).

BECAUSE THE EXACT CONSTRAINTS ARE UNIVERSAL, SCAN IS WIDELY PREDICTIVE. FOR EXAMPLE, IT WORKS WELL FOR THE DENSITY AND STRUCTURE OF LIQUID WATER, A DIFFICULT SYSTEM FOR WHICH MOST FUNCTIONALS FAIL (WU ET AL., IN PREPARATION). **SCAN IS THUS A POWERFUL AND COMPUTATIONALLY-EFFICIENT TOOL FOR MATERIALS DESIGN AND DISCOVERY.**

SCAN OFTEN PERFORMS LIKE A GOOD HYBRID FUNCTIONAL (HSE OR PBE0) , AT LOWER COMPUTATIONAL COST, AND PERFORMS BETTER THAN A HYBRID IN SYSTEMS WHERE VAN DER WAALS INTERACTION IS IMPORTANT.

THERE ARE STILL A FEW PROPERTIES FOR WHICH A GOOD HYBRID WILL OUTPERFORM SCAN: E.G., BARRIER HEIGHTS TO GAS-PHASE CHEMICAL REACTIONS, AND ENERGY GAPS OF SEMICONDUCTORS/INSULATORS.

NOW WE WILL DISCUSS THE BAND GAPS IN SCAN, EXPLAINING WHY THEY ARE BETTER THAN GGA BUT NOT AS GOOD AS HYBRID GAPS.

META-GGA's AND HYBRID FUNCTIONALS ARE ORBITAL FUNCTIONALS, AND ARE TYPICALLY IMPLEMENTED IN A *GENERALIZED* KOHN-SHAM (GKS) SCHEME, IN WHICH THE *MULTIPLICATIVE* KOHN-SHAM XC POTENTIAL IS REPLACED BY A DIFFERENTIAL OR INTEGRAL OPERATOR.

DOES META-GGA (E.G., SCAN) IMPROVE BAND GAPS OF REAL 3D SOLIDS, AND BY HOW MUCH? IF WE IMPLEMENT THE OEP CONSTRUCTION OF A MULTIPLICATIVE XC POTENTIAL WITHIN META-GGA, DO THE BAND GAPS GO BACK TO LSDA/GGA VALUES?

(YANG, PENG, SUN, & PERDEW, PHYS. REV. B (2016)).

WE HAVE COMPILED A DATA SET OF 26 SEMICONDUCTORS AND INSULATORS, AND PERFORMED GENERALIZED KOHN-SHAM BAND-STRUCTURE CALCULATIONS FOR THEM.

FOR SEMICONDUCTORS ($G < \sim 3$ eV), THE SCAN GKS BAND GAP g TYPICALLY CORRECTS ABOUT 40% OF THE GGA BAND GAP'S UNDERESTIMATION OF THE EXPERIMENTAL TOTAL-ENERGY GAP G .

WE ALWAYS FIND

$g(\text{LDA}) < \sim g(\text{GGA}) \sim g(\text{SCAN KS}) < \sim g(\text{SCAN GKS}) < \sim g(\text{HSE hyb}) < \sim G(\text{EXPT}).$

NOTE THAT THE MULTIPLICATIVE OPTIMIZED EFFECTIVE POTENTIAL FOR SCAN (CONSTRUCTED ONLY WITH MUCH EFFORT) YIELDS BAND GAPS g CLOSE TO THOSE OF GGA.

SOME TYPICAL RESULTS FOR BAND GAPS in eV

SOLID	LDA	PBE GGA	SCAN (KS) MGGA	SCAN (GKS) MGGA	HSE HYBRID	EXPT.
Si	0.60	0.71	0.78	0.97	1.11	1.17
CdSe	0.44	0.71	0.76	1.10	1.66	1.73
ZnS	1.87	2.12	2.16	2.63	3.32	3.72
MgO	4.70	4.74	4.80	5.62	6.46	7.90
Ar	8.44	8.92	8.89	9.91	10.33	14.3

WHILE GGA BAND GAPS OF THREE-DIMENSIONAL SEMI-CONDUCTORS ARE ONLY ABOUT 50% OF THE EXPERIMENTAL FUNDAMENTAL GAPS, META-GGA GAPS ARE ABOUT 70% IN GKS THEORY, BUT SIMILAR TO GGA IN OEP OR KS THEORY. THE GGA AND SCAN KS GAPS ARE PROBABLY CLOSE TO THE EXACT KOHN-SHAM BAND GAPS, WHICH WE KNOW UNDERESTIMATE THE TRUE GAPS BECAUSE OF THE DERIVATIVE DISCONTINUITY OF THE EXACT XC ENERGY. (PERDEW & LEVY 1983, SHAM & SCHLUETER 1983).

HYBRID GAPS (E.G., HSE) ARE CLOSER TO 100% FOR SEMICONDUCTORS, BUT ALSO UNDERESTIMATE THE GAPS FOR LARGE-GAP INSULATORS.

FUNDAMENTAL OR TOTAL-ENERGY GAP G OF A SOLID (ELECTRICALLY NEUTRAL WITH N ELECTRONS)

$E(M)$ = GROUND-STATE ENERGY OF SOLID WITH M ELECTRONS

$$G = I - A$$

$I = E(N-1) - E(N)$ = FIRST IONIZATION ENERGY OF NEUTRAL SOLID

$A = E(N) - E(N+1)$ = FIRST ELECTRON AFFINITY

SO THE EXPERIMENTAL GAP IS BOTH AN EXCITATION ENERGY OF THE NEUTRAL SYSTEM AND A GROUND-STATE ENERGY DIFFERENCE FOR ELECTRON REMOVAL AND ADDITION.

IF WE THINK OF THE FUNDAMENTAL GAP G AS AN EXCITATION ENERGY, WE HAVE NO REASON TO EXPECT THAT IT IS EQUAL TO THE BAND GAP g OF THE EXACT KOHN-SHAM POTENTIAL. BUT, IF WE THINK OF IT AS A GROUND-STATE ENERGY DIFFERENCE $I-A$, WE MIGHT HOPE THAT IT IS.

A.R. WILLIAMS AND U. VON BARTH 1983 GAVE A CLEAR ARGUMENT THAT IT IS. THEIR ARGUMENT WAS BASED ON THREE ASSUMPTIONS:

- (1) JANAK'S THEOREM: THE ORBITAL ENERGIES OF KOHN-SHAM THEORY ARE DERIVATIVES OF THE TOTAL ENERGY WITH RESPECT TO THE CORRESPONDING OCCUPATION NUMBER.
- (2) WHEN AN ELECTRON IS ADDED TO OR REMOVED FROM A SOLID (INFINITELY EXTENDED IN 1D, 2D, or 3D), THE DENSITY CHANGE IS INFINITESIMAL AND PERIODIC.

(3) WHEN AN ELECTRON IS ADDED OR REMOVED, THE KOHN-SHAM POTENTIAL CHANGES ONLY INFINITESIMALLY (IMPLICIT ASSUMPTION).

THE 1983 WORK OF J.P. PERDEW AND M. LEVY, AND OF L.J. SHAM AND M. SCHLUETER, SHOWED THAT ASSUMPTION (3) IS WRONG: SINCE THE EXACT KOHN-SHAM POTENTIAL MUST REPRODUCE THE EXACT GROUND-STATE DENSITY *AND* THE EXACT CHEMICAL POTENTIAL dE/dN , IT MUST JUMP UP BY A CONSTANT *DISCONTINUITY* WHEN AN ELECTRON IS ADDED TO A NEUTRAL SOLID. SO

$$G = g + x_c_DISCONTINUITY$$

NOTE THAT THE EXACT KOHN-SHAM POTENTIAL IS NOT A PHYSICAL OBJECT.

JANAK'S THEOREM CAN BE PROVED NOT ONLY WITHIN KS BUT ALSO WITHIN GKS THEORY.

FOR LSDA, GGA, OR STANDARD HYBRID FUNCTIONALS, THE DENSITY CHANGES INFINITESIMALLY WHEN AN ELECTRON IS ADDED TO OR REMOVED FROM A SOLID.

THE GKS POTENTIAL OPERATOR FOR ALL THESE FUNCTIONALS IS MANIFESTLY CONTINUOUS WHEN AN ELECTRON IS ADDED OR REMOVED. (FOR LDA AND GGA, GKS=KS.)

THEREFORE, THE WILLIAMS-VON BARTH ARGUMENT IS CORRECT WITHIN GKS!

GENERALIZED KOHN-SHAM BAND GAPS WITHIN A GIVEN APPROXIMATION ARE GROUND-STATE TOTAL ENERGY DIFFERENCES WITHIN THE SAME APPROXIMATION. (PERDEW ET AL. PNAS 2017)

NOW WE CAN UNDERSTAND WHY HYBRID FUNCTIONALS WITHIN A GKS SCHEME IMPROVE BAND GAPS, AND WHY THE SAME FRACTION OF EXACT EXCHANGE THAT IMPROVES TOTAL ENERGIES ALSO IMPROVES THE GAPS.

THE HYBRIDS YIELD THE RIGHT BAND GAPS FOR SEMICONDUCTORS FOR THE RIGHT REASON (ALTHOUGH ALL HYBRIDS ARE SOMEWHAT EMPIRICAL).

FOR MANY GROUND-STATE ENERGY DIFFERENCES, THE SCAN META-GGA PERFORMS LIKE A HYBRID, BUT NOT FOR BAND GAPS. WHY?

AN INSULATOR HAS A LONG-RANGE CONTRIBUTION TO THE EXCHANGE ENERGY THAT ARISES FROM IMPERFECT SCREENING, AND IS CAPTURED BY THE HYBRID FUNCTIONALS BUT NOT BY SEMILOCAL FUNCTIONALS INCLUDING SCAN. THIS LONG-RANGE CONTRIBUTION MIGHT CANCEL OUT OF GROUND-STATE ENERGY DIFFERENCES FOR WHICH THE ELECTRON NUMBER REMAINS CONSTANT, BUT NOT OUT OF THOSE FOR WHICH THE ELECTRON NUMBER CHANGES, E.G., I AND A.

SUMMARY

THE SCAN META-GGA IS WIDELY PREDICTIVE BECAUSE IT SATISFIES AS MANY EXACT CONSTRAINTS AS POSSIBLE. SCAN IS SOMETIMES MORE ACCURATE THAN A HYBRID FUNCTIONAL, AT LOWER COST.

WITHIN AND ONLY WITHIN A GENERALIZED KOHN-SHAM SCHEME, SCAN BAND GAPS FOR SOLIDS ARE MORE REALISTIC THAN GGA GAPS, BUT NOT AS ACCURATE AS HYBRID GAPS, BECAUSE SCAN IS A NEARLY-OPTIMAL SEMILOCAL FUNCTIONAL BUT NO SEMILOCAL FUNCTIONAL CAN CAPTURE THE LONG-RANGE PARTIALLY-SCREENED EXACT EXCHANGE FOUND IN SEMICONDUCTORS AND INSULATORS.