A FRESH LOOK AT THE BAND-GAP PROBLEM IN DENSITY FUNCTIONAL THEORY

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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

$G = 0$ FOR METALLIC CONDUCTION

$0<G<3$ eV FOR A SEMICONDUCTOR

VERY DIFFICULT TO EVALUATE G FROM I-A AS N->INFINITY, ESPECIALLY IN 3D.

EXPERIMENTALLY, THE FUNDAMENTAL GAP G IS THE UNBOUND LIMIT OF AN EXCITON SERIES.

EXCITONS OR BOUND ELECTRON- HOLE PAIRS CAN BE CREATED BY THE ABSORPTION OF PHOTONS.

SO THE TOTAL-ENERGY GAP G IS AN EXCITATION ENERGY AS WELL AS A SECOND DIFFERENCE OF GROUND-STATE ENERGIES.

THE GAP G CONTROLS THE TEMPERATURE DEPENDENCE OF THE INTRINSIC CONDUCTIVITY.
A DIRECT GAP G ALSO CONTROLS OPTICAL ABSORPTION.

KOHN-SHAM DENSITY FUNCTIONAL THEORY

W. KOHN AND L.J. SHAM 1965

A FORMALLY-EXACT WAY TO COMPUTE THE GROUND-STATE ENERGY AND ELECTRON DENSITY OF M COULOMB-INTERACTING ELECTRONS IN A MULTIPLICATIVE EXTERNAL POTENTIAL.

WE SET UP A FICTITIOUS SYSTEM OF NON-INTERACTING ELECTRONS WITH THE SAME GROUND-STATE DENSITY AS THE REAL INTERACTING SYSTEM. WE FIND THIS DENSITY BY SOLVING SELFCONSISTENT ONE-ELECTRON EQUATIONS. THE NON-INTERACTING ELECTRONS MOVE IN A MULTIPLICATIVE EFFECTIVE POTENTIAL CALLED THE KOHN-SHAM POTENTIAL.

CAN WE FIND THE FUNDAMENTAL ENERGY GAP G OF A SOLID AS THE BAND GAP g SEPARATING UNOCCUPIED FROM OCCUPIED ORBITALS IN THE BAND STRUCTURE OF THE EXACT KOHN-SHAM POTENTIAL FOR A NEUTRAL SOLID?

IN THE EARLY 1980’s, ONLY THE LOCAL SPIN DENSITY (LSDA) APPROXIMATION WAS AVAILABLE, BUT BAND STRUCTURE CALCULATIONS WERE ACCURATE ENOUGH TO SHOW THAT LSDA BAND GAPS g_LSDA WERE ON AVERAGE ONLY HALF THE MEASURED FUNDAMENTAL GAPS G FOR INSULATING SOLIDS.

WAS THIS A FAILURE OF THE LSDA EFFECTIVE POTENTIAL TO MIMIC THE EXACT KOHN-SHAM POTENTIAL, OR A FAILURE OF THE EXACT KOHN-SHAM POTENTIAL TO PREDICT THE FUNDAMENTAL GAP, OR BOTH?

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, 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, 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 1982 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

$$G = g + \text{DISCONTINUITY}$$

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

THIS ARGUMENT WAS SUPPORTED BY THE FACT THAT THE GGAs DEVELOPED LATER IMPROVED THE TOTAL ENERGY OVER LSDA, BUT LEFT THE BAND GAPS g OF SOLIDS ALMOST UNCHANGED. NEITHER LSDA NOR GGA HAS THE DERIVATIVE DISCONTINUITY OF THE EXACT FUNCTIONAL.

SINCE ABOUT 2000, IT HAS BECOME CLEAR THAT HYBRID FUNCTIONALS

AND DOUBLE HYBRIDS CAN YIELD MUCH MORE REALISTIC BAND GAPS FOR SOLIDS. THE HYBRIDS MIX SAY 25% OF HARTREE-FOCK EXCHANGE, 75% OF GGA EXCHANGE, AND 100% OF GGA CORRELATION, A COMBINATION THAT IMPROVES BOTH ENERGY DIFFERENCES AND BAND GAPS. BUT THE HYBRID XC POTENTIAL IS NOT A MULTIPLICATIVE OF KOHN-SHAM POTENTIAL, BECAUSE THE HARTREE-FOCK EXCHANGE POTENTIAL IS NOT.

GENERALIZED KOHN-SHAM (GKS) THEORY

THE HYBRID FUNCTIONALS ARE EXAMPLES OF “GKS THEORY”:

START FROM A RIGOROUS KS DENSITY FUNCTIONAL THEORY. IN THIS THEORY, THE KS ORBITALS ARE FUNCTIONALS OF THE DENSITY. ONE CAN CONSTRUCT THE XC ENERGY RIGOROUSLY FROM THESE ORBITALS.

TO REMAIN IN KS THEORY, WE WOULD HAVE TO USE THE OPTIMIZED EFFECTIVE POTENTIAL (OEP) METHOD TO FIND THE MULTIPLICATIVE OR KS XC POTENTIAL THAT MINIMIZES THE ENERGY AS A FUNCTIONAL OF THESE ORBITALS. INSTEAD, WE TAKE A SMALL STEP OUT OF KS THEORY BY FINDING THE NON-MULTIPLICATIVE XC POTENTIAL THAT MINIMIZES THE ENERGY AS A FUNCTIONAL OF THE ORBITALS.

FOR EXAMPLE, THE HARTREE-FOCK EXCHANGE POTENTIAL IS NOT A MULTIPLICATION OPERATOR BUT A LINEAR HERMITIAN INTEGRAL OPERATOR.

WE KNOW THAT THE TOTAL ENERGY IS ALMOST UNCHANGED FROM KS TO GKS, WHILE THE ORBITAL ENERGIES ARE SERIOUSLY CHANGED.

AVOIDING THE OEP CONSTRUCTION OF THE KS POTENTIAL NOT ONLY SAVES A HUGE AMOUNT OF COMPUTATION TIME, BUT FOR THE HYBRIDS IT EVEN MAKES THE GKS BAND GAPS “PHYSICAL” OR CLOSE TO THE FUNDAMENTAL GAP.

WHY?

WE HAVE RECENTLY FOUND THE ANSWER:

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.

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

CAN WE FIND THE FUNDAMENTAL OR TOTAL-ENERGY GAP G BY EVALUATING THE BAND GAP g = LOWEST-UNOCCUPIED – HIGHEST-OCCUPIED BAND OR ORBITAL ENERGY IN DENSITY FUNCTIONAL THEORY?

THE ANSWER IS YES WITHIN TYPICAL APPROXIMATIONS TO THE EXCHANGE-CORRELATION (XC) ENERGY AS A FUNCTIONAL OF THE ELECTRON DENSITY OR OCCUPIED ORBITALS, E.G.,

LOCAL SPIN DENSITY APPROXIMATION (LSDA),

GENERALIZED GRADIENT APPROXIMATION (GGA),

META-GGA,

HYBRID OF GGA WITH EXACT EXCHANGE,

IF WE USE THE OPTIMUM VARIATIONAL XC POTENTIAL (GENERALIZED KOHN-SHAM SCHEME). THIS IS A MULTIPLICATIVE POTENTIAL FOR LSDA OR GGA, BUT NOT FOR A HYBRID FUNCTIONAL.

THESE CONCLUSIONS ABOUT THE META-GGA AND HYBRID GAPS ARE ALSO BY THEMSELVES IMPLIED BY THE MORE-GENERAL GKS THEOREMS OF YANG, MORI-SANCHEZ, AND COHEN 2008-2012.

BUT THE ANSWER IS NO IF WE USE THE EXACT XC ENERGY WITHIN AN UNGENERALIZED KOHN-SHAM SCHEME, AS A CONSEQUENCE OF THE DISCONTINUITY IN THE EXACT KOHN-SHAM XC POTENTIAL.

(PERDEW, PARR, LEVY, AND BALDUZ 1982).

G=g AND BOTH ARE UNDERESTIMATED BY ABOUT 50% IN LDA & GGA,

IN COMPARISON WITH THE EXPERIMENTAL G.

THE EXACT UNGENERALIZED KOHN-SHAM g ALSO UNDERESTIMATES THE EXPERIMENTAL G ABOUT 50%.

WE CAN GET MUCH MORE ACCURATE G=g WITHIN A GENERALIZED KOHN-SHAM SCHEME, IN WHICH THE XC POTENTIAL IS A HERMITEAN BUT NON-MULTIPLICATIVE OPERATOR

FAMILIAR EXAMPLE: HYBRID OF GGA WITH EXACT EXCHANGE

(INTEGRAL OPERATOR)

THE HYBRID GAPS ARE RATHER REALISTIC, BUT ALL HYBRID FUNCTIONALS ARE SOMEWHAT EMPIRICAL, AND COMPUTATIONALLY EXPENSIVE.

UNFAMILIAR EXAMPLE: META-GGA (DIFFERENTIAL OPERATOR)

NUMERICAL CONFIRMATION

WE CONSIDER A FINITE LINEAR CHAIN OF H2 MOLECULES, WHERE THE SEPARATION BETWEEN THE NUCLEI OF NEIGHBORING MOLECULES IS 1.25 TIMES THE SEPARATION BETWEEN NUCLEI WITHIN A MOLECULE. WE CONSIDER CHAINS WITH 1 TO 500 MOLECULES, AND EXTRAPOLATE CAREFULLY TO AN INFINITE NUMBER.

FUNCTIONAL	G	g	(eV)
LDA	2.98	2.96	
PBE	3.15	3.13	
SCAN	3.32	3.29	
HSE06	4.21	4.18	

SUMMARY:

GENERALIZED KOHN-SHAM BAND GAPS WITHIN A GIVEN APPROXIMATION ARE GROUND-STATE TOTAL ENERGY DIFFERENCES WITHIN THE SAME APPROXIMATION.

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.

META-GGA’s ARE ALSO ORBITAL FUNCTIONALS, AND ARE IMPLEMENTED IN A GKS SCHEME. META-GGA ENERGIES CAN BE BETTER THAN GGA, AND SOMETIMES COMPARABLE TO OR BETTER THAN HYBRID ENERGIES, AT LOWER COMPUTATIONAL COST.

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?

Z. YANG, H. PENG, J. SUN, AND J.P. PERDEW, PHYSICAL REVIEW B **93**, 205205 (2016).

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

THE SCAN BAND GAP TYPICALLY CORRECTS ABOUT HALF OF THE GGA BAND GAP's UNDERESTIMATION OF THE EXPERIMENTAL TOTAL-ENERGY GAP.

WE ALWAYS FIND

g(GGA) <~ g(SCAN) <~ G(EXPT)

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

DISAPPOINTMENTS:

THE BAND GAP g IS ZERO IN BOTH GGA AND SCAN FOR 3 SEMICONDUCTORS: Ge, InN, CdO.

PLEASANT SURPRISE: WHILE THE BAND GAP g IS ZERO IN GGA FOR THE BETA STRUCTURE OF MnO2, IT IS CLOSE TO EXPERIMENT IN SCAN FOR BOTH STRUCTURES WHERE AN EXPERIMENTAL VALUE EXISTS:

Crystal structure	g(SCAN) (eV)	G(EXPT) (eV)
Beta (g.s.)	0.4	0.3
Delta (layered)	2.0	2.1

ONLY FOR MnO2 HAVE WE FOUND THIS SO FAR.

SUMMARY

WHILE LDA AND GGA BAND GAPS OF THREE-DIMENSIONAL SOLIDS ARE ONLY ABOUT 50% OF THE EXPERIMENTAL FUNDAMENTAL GAPS, META-GGA GAPS ARE ABOUT 70% IN GKS THEORY, BUT SIMILAR TO LDA AND GGA IN OEP OR KS THEORY.

HYBRID GAPS (E.G., HSE06) ARE CLOSER TO 100%.