



TECHNICAL UNIVERSITY OF KENYA

Education and Training for the Real World



Exchange and Correlation Functionals

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Presentation outline

- Talk motivation
- Brief review on Hartree-Fock (HF) and Kohn-Sham (KS) DFT
- Some existing information on functionals
- Definitions and terms
- Types of Exchange-Correlation (XC) functionals
- Results on use of various XC functionals
- Additional references and sources
- Acknowledgement

Talk motivation

- Provide foundational information on XC functionals - conceptual emphasis
- The significance of XC functionals
- Basis of choice of XC functionals to employ in problems of interest
- LDA and GGA XC functionals and existing resources for use

Brief review on Hartree-Fock (HF) and Kohn-Sham (KS) DFT

- HF theory employs antisymmetric wavefunctions for electrons; ground state calculations – use of a single Slater determinant wavefunction
- HF calculations are static omitting aspects of correlation and exchange
- HF equations are solved self consistently within a predetermined tolerance

Brief review on Hartree-Fock (HF) and Kohn-Sham (KS) DFT

- In restricted HF, the Fock operator is given by

$$\hat{f}_{\text{HF}}(1) = \hat{h}(1) + \sum_{j=1}^{N/2} 2\hat{J}_j(1) - \sum_{j=1}^{N/2} \hat{K}_j(1)$$

- Term 1 on the RHS is the core Hamiltonian, 2nd and 3rd are the Coulomb and exchange terms
- HF equations are self-interaction free
- However, HF calculations are only practical for systems with a few electrons

Brief review on Hartree-Fock (HF) and Kohn-Sham (KS) DFT

- KS DFT employs an auxiliary (fictitious) system of non-interacting electrons with the same electron density as the problem under investigation
- The auxiliary system is solved self consistently at a reduced cost enabling studies of systems with many electrons
- On implementation, exchange and correlation (XC) functionals are needed

Brief review on Hartree-Fock (HF) and Kohn-Sham (KS) DFT

Energy in KS-DFT $E_{\text{KS}}[\rho] = T_{\text{ref}}[\rho] + V_{\text{eN}}[\rho] + J[\rho] + E_{\text{XC}}[\rho]$

$$T_{\text{ref}}[\rho] = \sum_{i=1}^{N/2} 2 \left\langle \psi_i^{\text{KS}} \left| -\frac{1}{2} \nabla^2 \right| \psi_i^{\text{KS}} \right\rangle$$

$V_{\text{eN}}[\rho]$ – electron - nucleus interaction

The KS wavefunction is a single Slater determinant of the KS orbitals denoted by $\psi_{\text{ref}} = \psi_{\text{KS}}$

$$J[\rho] = \frac{1}{2} \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

$$E_{\text{XC}}[\rho] = \left(T[\rho] - T_{\text{ref}}[\rho] \right) + \left(V_{\text{ee}}[\rho] - J[\rho] \right)$$

$T[\rho]$ – actual electrons KE
 $V_{\text{ee}}[\rho]$ – actual electron-electron interaction

Choice of the KS orbitals is such that electron density of reference is equal that of system under study

Brief review on Hartree-Fock (HF) and Kohn-Sham (KS) DFT

KS 'Fock' operator

$$\hat{f}_{\text{KS}}(\vec{r})\psi_i^{\text{KS}}(\vec{r}) = \epsilon_i^{\text{KS}}\psi_i^{\text{KS}}(\vec{r})$$

$$\hat{f}_{\text{KS}}(1) = -\frac{1}{2}\nabla^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}} + \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{\text{XC}}(\vec{r}_1) \quad V_{\text{XC}}(\vec{r}) = \frac{\delta E_{\text{XC}}[\rho]}{\delta \rho(\vec{r})}$$

In restricted HF (RHF)

$$\hat{f}_{\text{HF}}(1) = \hat{h}(1) + \sum_{j=1}^{N/2} 2\hat{J}_j(1) - \sum_{j=1}^{N/2} \hat{K}_j(1)$$

First two terms in KS 'Fock' operator represented by the core Hamiltonian $h(1)$ in RHF. Third term in KS 'Fock' operator equivalent to the Coulomb term in RHF

The Fock operators are similar except for the V_{XC} potential in the KS DFT formulation

V_{XC} potential is expected to include correlation and exchange effects not considered by HF

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Some existing information on XC functionals

- It is estimated that 500 – 600 XC functionals have been developed to date
- Functionals developed for specific problems may be limiting on a wider scope; choice between accuracy and universal applicability arises
- Determination of band gaps in materials has seen development of large numbers of XC and trends due applications in photoelectronic as well as photovoltaic technology

Some existing information on XC functionals

- Knowledge of the performance of a XC functional in a wide array of compounds may serve as a guide for choice
- Quality of results obtained depend on the type of XC functional employed; choice should be guided by tests on the problem
- It is recommended that a XC functional working well for a small system be tested as a function of system size where applicable

Some existing information on XC functionals

XC functional flavours [Rappoport et al (2008)]

- Non-empirical: not fit to material properties; have systematic errors hence some predictability (LDA, GGA) - have wider use
- A few accurately known fit parameters are used: no parameters for system under study, unreliable for new systems due unsystematic errors
- Too many fit parameters used: may not be appropriate

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Definitions and terms

Electron correlation:

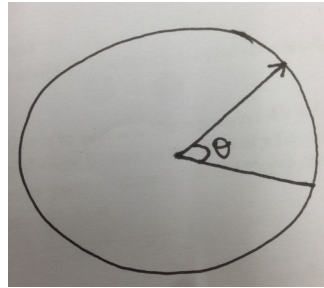
Describes how the motion an electron affects other electrons in a system (static or dynamical)

Exchange

Arises from the requirement that electron wavefunctions are antisymmetric as proposed by Slater (Slater determinant)

Definitions and terms

A functional assigns a number to a function; consider a 2D closed curve with an area $A[r]$ and perimeter $P[r]$



The area $A[r] = \int_0^{2\pi} d\theta f(r(\theta))$ is a local functional of r as it is the only quantity needed in the integrand to find area

The perimeter $P[r] = \int_0^{2\pi} d\theta \times \sqrt{r^2(\theta) + \left(\frac{dr}{d\theta}\right)^2}$ is said to be a

semi-local functional of r since $r(\theta)$ and $dr/d\theta$

are both needed to find the perimeter

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Types of XC functional – LDA

Homogeneous gas

- XC energy per particle of the infinite uniform electron gas with density ρ

$$E_{xc}^{\text{LDA}}[\rho] = \int \rho(\vec{r}) \epsilon_{xc}^{\text{unif}}(\rho(\vec{r})) d\mathbf{r}$$

Inhomogeneous gas

- no uniformity in general (atoms, molecules); high density gradients are present around nuclei

- XC energy per particle at a point r with density $\rho(\vec{r})$, is approximated to be that of the uniform electron gas of the same density

Types of XC functional – LDA

$$\epsilon_{xc}^{\text{unif}}(\rho) = \epsilon_x^{\text{unif}}(\rho) + \epsilon_c^{\text{unif}}(\rho)$$

only electron density at a point needed - local

exchange functional energy per particle is given by

$$\epsilon_x^{\text{unif}}[\rho] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \rho^{1/3}$$

• the correlation functional has no analytical form; numerical QMC calculations needed for $\rho(\vec{r})$ with fitting to high and low limits, respectively, as:

$$\epsilon_c^{\text{unif}} = A \ln r_s + B + C r_s \ln r_s + O(r_s) \quad \epsilon_c^{\text{unif}} = \frac{a}{r_s} + \frac{b}{r_s^{3/2}} + O(1/r_s)$$

$$r_s = \left(\frac{3}{4\pi\rho} \right)^{1/3}$$

Common LDA parametrization – Perdew and Wang (PW92)
[PRB35, 13244, 1992]

Types of XC functional – GGA

- Generalized Expansion Approximation (GEA) was developed to improve LDA:

$$E_{\text{xc}}^{\text{GEA}}(\rho) = \int d^3\vec{r} \varepsilon_{\text{xc}}^{\text{LDA}}[\rho] \rho(\vec{r}) \left[1 + C \left(\frac{\vec{\nabla} \rho(\vec{r})}{2k_F(\vec{r}) \rho(\vec{r})} \right) \right]$$

$$k_F(\vec{r}) = (3\pi^2 \rho(\vec{r}))^{1/3}$$

GEA did not perform better than LDA as it violated XC hole sum rules:

$$\int \rho_c(\vec{r}, \vec{r}') d^3\vec{r}' = 0 \qquad \rho_x(\vec{r}, \vec{r}') \leq 0$$

Types of XC functional – GGA

- Generalized Gradient Approximation (GGA) was developed with preservation of XC hole sum rules:

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

both the electron density and gradient of electron density at a point needed - semi-local

Most implemented GGA is by Perdew-Burke-Erzerhof [PRL 77, 3865 (1996)]

$$E_x^{\text{GGA}} = \int d^3\vec{r} \rho(\vec{r}) \varepsilon_x^{\text{unif}}(\rho) F_x^{\text{PBE}}(s) \quad s = \frac{|\vec{\nabla}\rho|}{2k_F\rho}$$

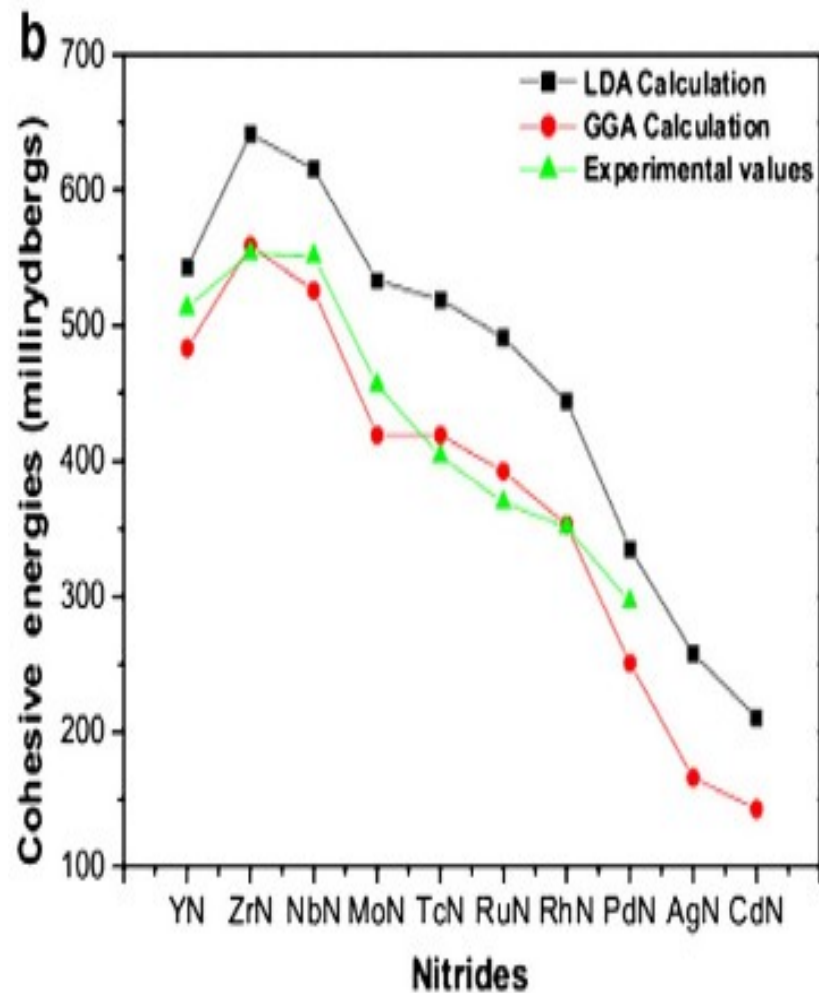
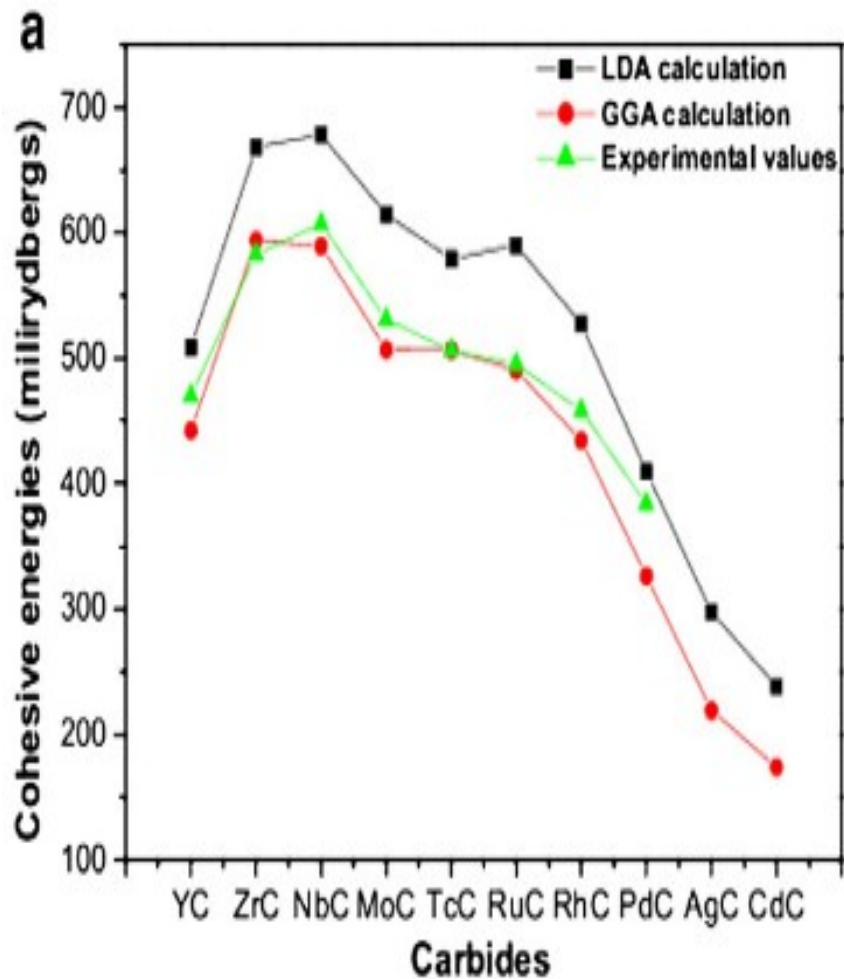
$$E_C^{\text{GGA}} = \int d^3\vec{r} \rho(\vec{r}) \left[\varepsilon_c^{\text{unif}}(\rho) + H^{\text{PBE}}(r_s, t) \right]$$

$$t = \frac{|\nabla\rho|}{2k_s\rho} \quad k_s = \left(\frac{4k_F}{\pi} \right)^{1/2}$$

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Results on use of various XC functionals



GGA results are closer to available experimental data

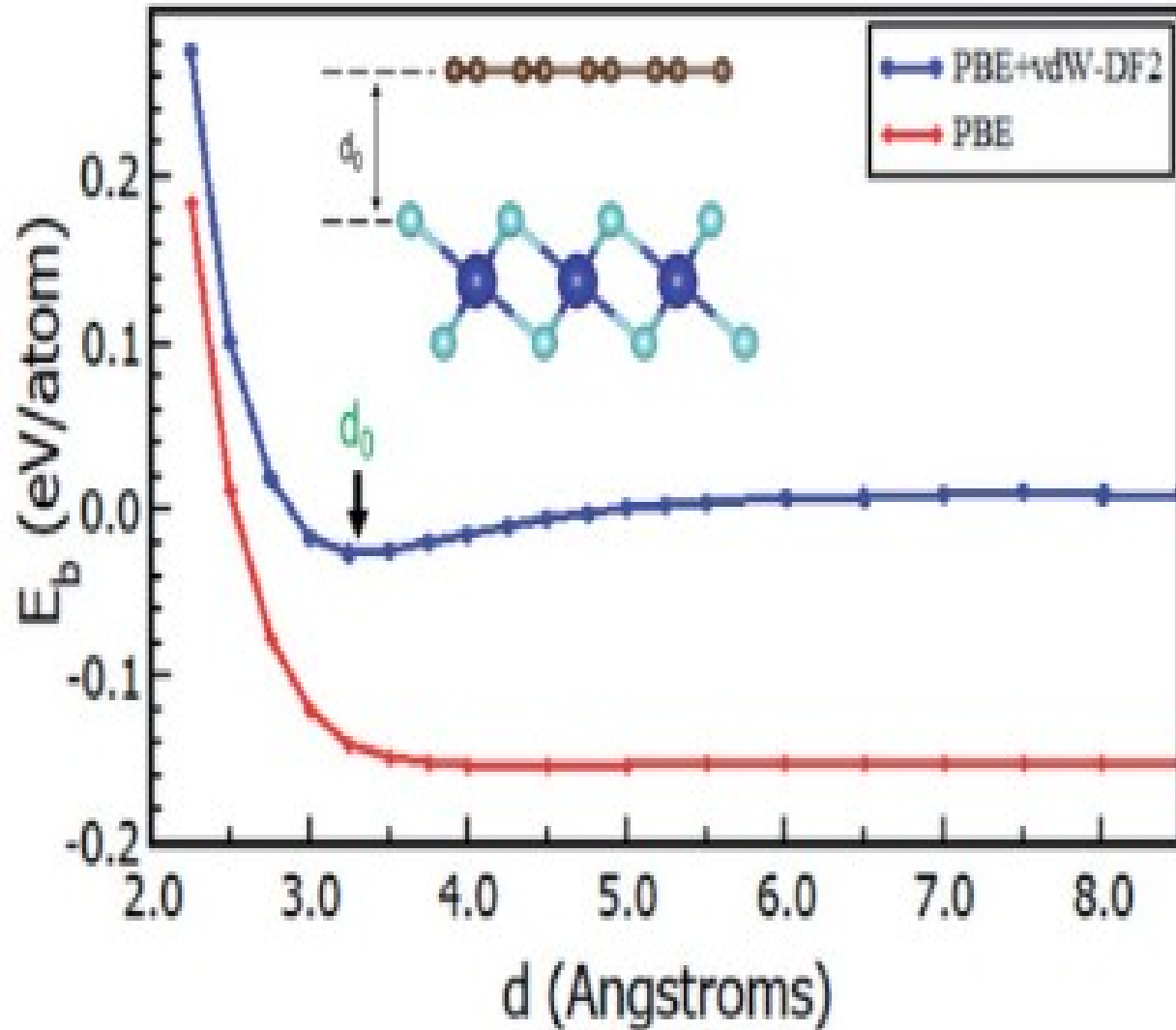
Results on use of various XC functionals

KCuO ₂				RbCuO ₂			
	PBE	PBEsol	Expt. [20]		PBE	PBEsol	Expt. [20]
<i>a</i>	4.568 (4.3%)	4.496 (2.8%)	4.375		4.967 (4.4%)	4.864 (2.3%)	4.756
<i>b</i>	11.731 (0.3%)	11.544 (1.3%)	11.696		12.013 (0.5%)	11.722 (-2.0%)	11.957
<i>c</i>	5.524 (2.0%)	5.436 (0.4%)	5.414		5.542 (2.5%)	5.434 (0.5%)	5.409
<i>V</i> ₀	296.016 (6.9%)	282.138 (1.8%)	277.034		330.701 (7.5%)	309.823 (0.7%)	307.596
<i>B</i> ₀	25.88	26.09	-		24.91	25.33	-
<i>B</i> ' ₀	3.89	3.51	-		4.25	4.063	-

CsCuO ₂			
	PBE	PBEsol	Expt. [20]
	5.422 (3.2%)	5.227 (-0.5%)	5.254
	12.286 (1.3%)	11.962 (1.4%)	12.128
	5.563 (3.4%)	5.443 (1.2%)	5.38
	370.578 (8.2%)	340.326 (-0.7%)	342.816
	24.01	24.15	-
	4.99	6.12	-

PBEsol results are, in a majority of cases, closer to available experimental data

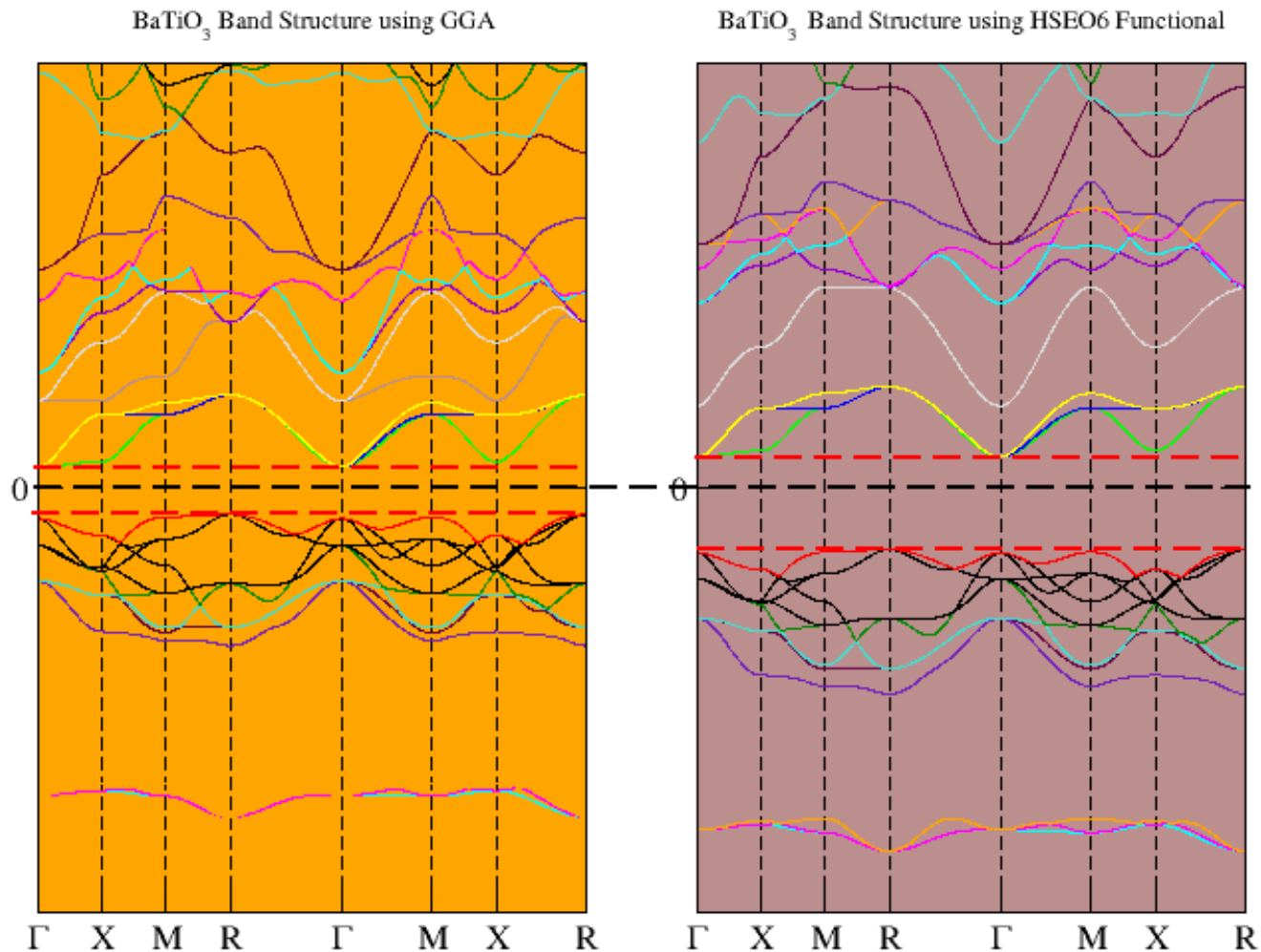
Results on use of various XC functionals



Use of PBE alone does not produce expected trend

Gr-HfS2: *RSC Adv.* 2020 10 30127- King'ori et al

Results on use of various XC functionals



HSE functional results open up the band gap despite additional computational expense
(work in progress using the Siesta code)

Additional references and resources:

Marques and Burnus in *Computer Physics Communications* 183, 10 (2012)

Libxc: a library of exchange and correlational Functionals – (seek latest information)

Cohen, Mori-Sanchez and Yang, *Chemical Reviews* (2012);

Borlido et al, *Nature Physics Journal* (2020)

Rappoport et al, ‘Which functional should I use?’ (2008)

Additional references and resources

Lectures by Stephan P A Sauer – Advanced Quantum Chemistry

ABC of DFT – Kieron Burke and friends (2007)

Selected common XC functionals (Rappoport et al 2008)

X: exchange functional

C: Correlation functional

Functional	Authors
Local Density Approximation (LDA)	
PZ81	Perdew and Zunger
PW92	Perdew and Wang
SVWN	X: Slater C: Vosko, Wilk and Nusair
Generalized Gradient Approximation (GGA)	
PW91	Perdew and Wang
PBE	Perdew, Burke and Enzerhof
PBEsol	Perdew, Ruzsinsky et al

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