Assessment of numerical behaviors of the R2SCAN exchange-correlation functional*

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➔Lessons learned while implementing and testing the ABINIT software package with the R2SCAN (Furness, 2020) exchange-correlation functional using "generalized" Kohn-Sham equations and the Projector Augmented Wave (PAW) formalism (Blöchl, 1994)

➔Question: For reliable numerical evaluation of generalized Kohn-Sham equations within plane wave codes such as ABINIT, is it important/necessary to use pseudopotential datasets explicitly generated using the R2SCAN functional?

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Outline of presentation

- ❑ History and literature results based on the VASP software package
- ❑ Basic equations and implementation in the ABINIT software package
  - ➢ Generation of pseudopotential datasets using ATOMPAW software for R2SCAN (actually R2SCAN01) (Holzwarth, Torrent, 2022)
  - ➢ Details of structural optimization
- ❑ Test results
  - ➢ Simple binary materials
  - ➢ More complicated structures
- ❑ Conclusions

- History and literature results
  - Systematic improvement of exchange-correlation functionals to the so-called meta-GGA form
    - "SCAN" – "Strongly Constrained and Appropriately Normed Semilocal Density Functional" Jianwei Sun, Adrienn Ruzsinszky, and John P. Perdew, PRL (2015)
    - "R2SCAN" – "Accurate and Numerically Efficient r2SCAN Meta-Generalized Gradient Approximation" James W. Furness, Aaron D. Kaplan, Jinliang Ning, John P. Perdew, and Jianwei Sun, JPCL (2020)
  - Performance studies on large varieties of materials using R2SCAN functional using the VASP code – for example –
    - (Kothakonda, 2022) Good structure and energetics
    - (Ning, 2022) Good lattice dynamics
    - (Furness, 2022) Careful numerical analysis especially for atomization energies, concluding that "The greater smoothness of r2SCAN seems to lead to better general accuracy than the additional exact constraint of SCAN or r4SCAN does."

❑ Basic equations

In terms of single particle states $\Phi_i(\mathbf{r})$ having occupancy w_i,

$$n(\mathbf{r}) \equiv \sum_i w_i \left|\Phi_i(\mathbf{r})\right|^2 \qquad \sigma(\mathbf{r}) \equiv \nabla n(\mathbf{r}) \cdot \nabla n(\mathbf{r}) \qquad \tau(\mathbf{r}) = \frac{\hbar^2}{2m} \sum_i w_i \left|\nabla \Phi_i(\mathbf{r})\right|^2,$$

General form of the exchange-correlation functional: $E_{xc} = \int d^3r \, f_{xc}(n(\mathbf{r}), \sigma(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r}))$

LDA GGA meta-GGA

The generalized Kohn-Sham equation takes the form: $H(\mathbf{r})\Phi_i(r) = \varepsilon_i \Phi_i(r)$

$$H(\mathbf{r}) = -\frac{\hbar^2}{2m}\left(\nabla^2 + \nabla \cdot \left(V_\tau(\mathbf{r})\nabla\right)\right) + V_{\text{eff}}(\mathbf{r}) \qquad V_{\text{eff}}(\mathbf{r}) = V_{\text{electron-nucleus}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{xc}(\mathbf{r})$$

$$V_\tau(\mathbf{r}) \equiv \frac{\partial f_{xc}}{\partial \tau} \qquad V_{xc}(\mathbf{r}) = \frac{\partial f_{xc}}{\partial n} - \nabla \cdot \left(2\frac{\partial f_{xc}}{\partial \sigma}\nabla n\right) + \nabla^2\left(\frac{\partial f_{xc}}{\partial\left(\nabla^2 n\right)}\right)$$

The presence of $\tau(\mathbf{r})$ in the energy requires additional terms in the evaluation of forces and stresses.

Steps needed to implement a new exchange-correlation functional into an electronic structure code such as ABINIT –

A. Create a pseudopotential dataset for the functional for each atom of interest
B. Adjust the electronic structure code as needed for the new functional
C. Test

Note that some of this work can be greatly facilitated with the use of the Libxc software package, as explained by (Lehtola and Marques, 2023)

Implemented in the ATOMPAW code (Holzwarth, Torrent, ..,2022)

Implemented in the ABINIT code V 10.2.7

Question: It is our understanding that step A is not always done and was not done in the literature studies using VASP

Is it really necessary?

❑ Test procedures

Two exchange-correlation functionals were compared

- PBESOL (Perdew,Ruzsinszky,..,2008)
- R2SCAN01 (Furness, 2020)

For each atomic species in the study ATOMPAW was used to generate PAW atomic datasets for PBESOL and for R2SCAN01

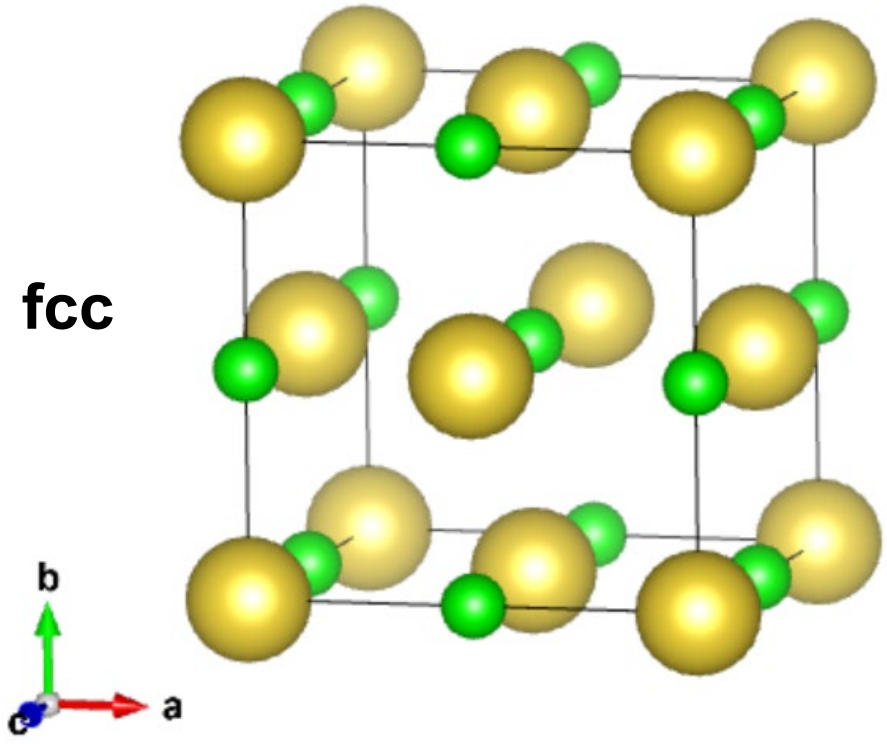
For each material studied, ABINIT was run with three steps:

Step 1: Using PBESOL functional only -- PBESOLwPBESOL
Step 2: Using R2SCAN01 with PBESOL datasets – R2SCAN01wPBESOL
Step 3: Using R2SCAN01 functional only -- R2SCAN01wR2SCAN01

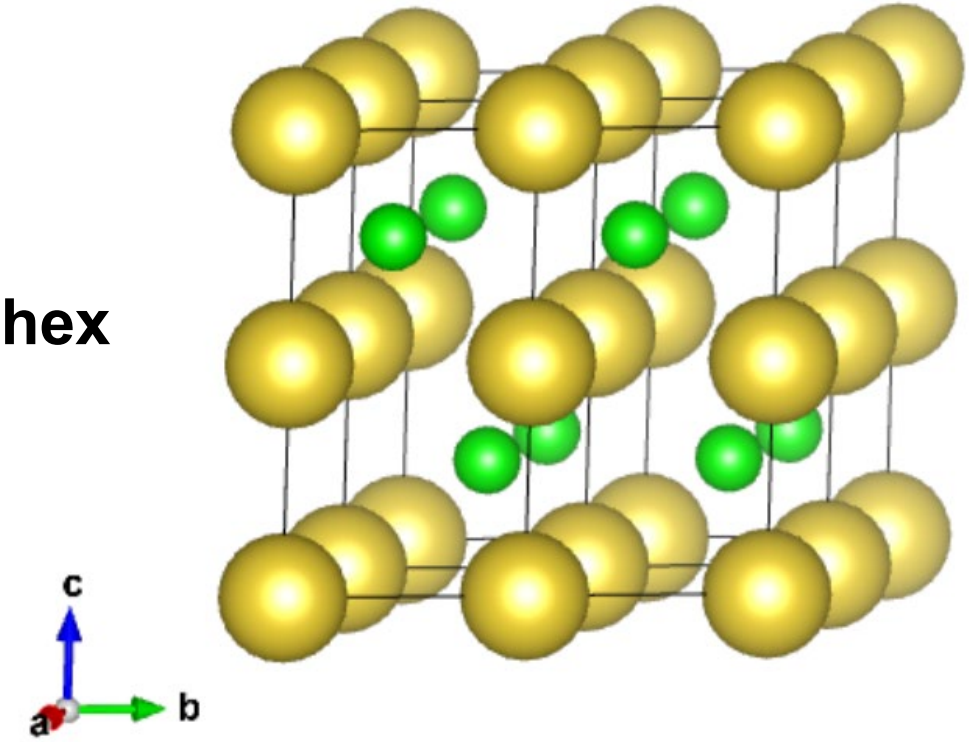
For efficiency: Step 2 iterations used Step 1 wavefunctions
Step 3 iterations used Step 2 wavefunctions

Study of 6 examples of ionic binary materials in their fcc (Fm-3m) and hex (P63/mmc) structures

fcc



hex



Using initial structures from OQMD from Northwestern U. https://oqmd.org/

ABINIT parameters: ionmov=2 tolvrs=1.d-12 tolmxf=1.d-8 ecut=42 Ha

	fcc	hex	ΔE/FU
LiF			
PBESOLwPBESOL	a = 2.83 Å	a = 2.78 Å c=4.99 Å	0.21 eV
R2SCAN01wPBESOL	a = 2.82 Å	a = 2.77 Å c=4.98 Å	0.24 eV
R2SCAN01wR2SCAN01	a = 2.85 Å	a = 2.80 Å c=5.00 Å	0.23 eV

	fcc	hex	ΔE/FU
LiCl			
PBESOLwPBESOL	a = 3.58 Å	a = 3.51 Å c=6.46 Å	0.21 eV
R2SCAN01wPBESOL	a = 3.63 Å	a = 3.56 Å c=6.54 Å	0.23 eV
R2SCAN01wR2SCAN01	a = 3.61 Å	a = 3.55 Å c=6.56 Å	0.22 eV

	fcc	hex	ΔE/FU
NaF			
PBESOLwPBESOL	a = 3.28 Å	a = 3.20 Å c=5.64 Å	0.12 eV
R2SCAN01wPBESOL	a = 3.25 Å	a = 3.18 Å c=5.61 Å	0.13 eV
R2SCAN01wR2SCAN01	a = 3.28 Å	a = 3.20 Å c=5.68 Å	0.11 eV

	Fcc	hex	ΔE/FU
NaCl			
PBESOLwPBESOL	a = 3.97 Å	a = 3.86 Å c=6.99 Å	0.11 eV
R2SCAN01wPBESOL	a = 3.99 Å	a = 3.89 Å c=7.04 Å	0.14 eV
R2SCAN01wR2SCAN01	a = 4.02 Å	a = 3.93 Å c=7.06 Å	0.14 eV

	fcc	hex	ΔE/FU
MgO			
PBESOLwPBESOL	a = 2.98 Å	a = 2.93 Å c=5.19 Å	0.49 eV
R2SCAN01wPBESOL	a = 2.98 Å	a = 2.93 Å c=5.18 Å	0.54 eV
R2SCAN01wR2SCAN01	a = 3.00 Å	a = 2.94 Å c=5.18 Å	0.55 eV

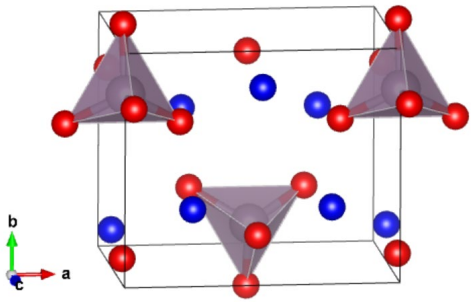
:	Fcc	hex	ΔE/FU
MgS			
PBESOLwPBESOL	a = 3.67 Å	a = 3.59 Å c=6.52 Å	0.49 eV
R2SCAN01wPBESOL	a = 3.68 Å	a = 3.60 Å c=6.54 Å	0.54 eV
R2SCAN01wR2SCAN01	a = 3.73 Å	a = 3.65 Å c=6.57 Å	0.53 eV

Study of optimized structures of ionic conductors Li_3PO_4 and Li_3PS_4 in their Pmn21 and Pmna structures

Li_3PO_4

Li_3PS_4

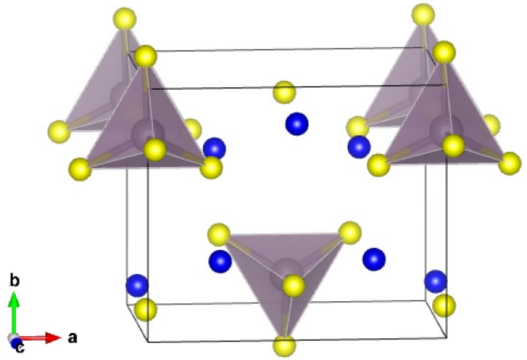
Pmn21



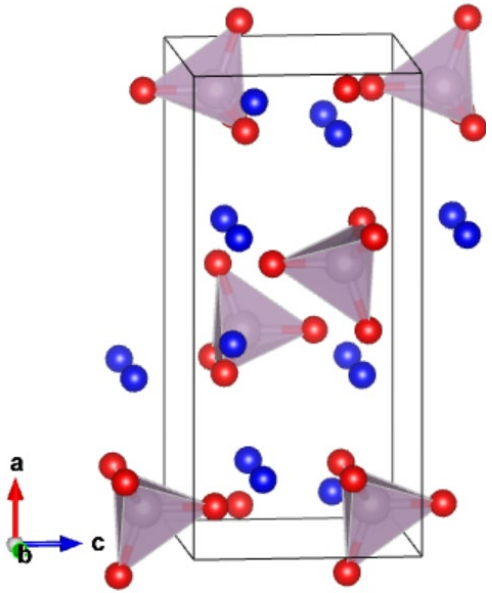
Li

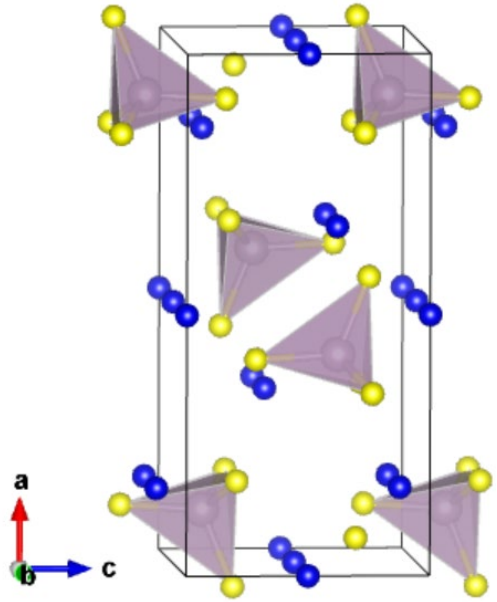
PO_4

PS_4



Pnma





Summary of results – comparing Li_3PO_4 and Li_3PS_4

		Pmn21			Pnma			
		a (Å)	*b* (Å)	*c* (Å)	*a* (Å)	*b* (Å)	*c* (Å)	ΔE (eV/FU)
Li_3PO_4	Exp[1]	6.12	5.25	4.87	10.47	6.11	4.92	
	PBESOLwPBESOL	6.10	5.23	4.84	10.47	6.10	4.92	0.02
	R2SCAN01wPBESOL	6.09	5.22	4.84	10.45	6.10	4.90	0.02
	R2SCAN01wR2SCAN01	6.09	5.23	4.87	10.48	6.10	4.94	0.02
Li_3PS_4	Exp[2]	7.71	6.54	6.14	12.89	8.22	6.12	
	PBESOLwPBESOL	7.68	6.54	6.14	13.02	7.97	6.08	0.04
	R2SCAN01wPBESOL	7.73	6.58	6.19	13.06	8.04	6.20	0.08
	R2SCAN01wR2SCAN01	7.75	6.61	6.19	13.08	8.05	6.19	0.06

ABINIT parameters: ionmov=2 toldff=1.d-7 tolmxf=1.d-5 ecut=42 Ha

Conclusions –

➔**Question:** For reliable numerical evaluation of generalized Kohn-Sham equations within plane wave codes such as ABINIT, is it important/necessary to use pseudopotential datasets explicitly generated using the R2SCAN functional?

➔**Answer:** Maybe? Our current surveys using the Projector Augmented Wave methodology with strict tolerances, show small differences between R2SCAN01wPBESOL and R2SCAN01wR2SCAN01 structure and energy results, marginally above typical general computational errors. We have yet to find an an example exhibiting large differences.

➔**Opinion:** In order to maintain confidence in computational results, it is important to have multiple independent codes. Much appreciation is extended to those who develop and share their codes and collaborate with users.

Thank you for listening.

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Patrizia Calaminici, CINVESTAV, Centro De Investigacion
Marcio Costa, Fluminense Federal University
Pierre Darancet, Argonne National Laboratory
Robert DiStasio, Cornell University
Chad Hoyer, The University of Texas at El Paso
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Scott Jensen, University of Louisville
Daniel Kaplan, Rutgers, The State University of New Jersey
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Winfred Mulwa, Egerton University, Kenya
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Extra slides

The R2SCAN formulation includes the $\tau(\boldsymbol{r})$ dependence using the following functional form:

$$\bar{\alpha} \equiv \frac{\tau - \tau_W}{\tau_{\text{unif}} + \eta\tau_W} \qquad \tau_W = \frac{|\nabla n|^2}{8n} \qquad \tau_{\text{unif}} = \frac{3n}{10}\left(3\pi^2 n\right)^{2/3}$$

$$\text{R2SCAN:} \quad \eta = 0.001$$

$$\text{R2SCAN01:} \quad \eta = 0.01$$