SIMPLIFICATION OF META-GGA EXCHANGE-CORRELATION FUNCTIONALS

Samuel B. Trickey

Quantum Theory Project
Physics, Chemistry - University of Florida

trickey@qtp.ufl.edu
www.qtp.ufl.edu/ofdft

XXVII IMRC, 21 Aug. 2018

Univ. Florida Free-energy DFT & Orbital-Free DFT Group

Sam Trickey, Jim Dufty

Kai Luo, Daniel Mejía Rodríguez, Jeffrey Wrighton

Affiliates: Frank Harris (U. Utah); Keith Runge (U. Arizona)

Alumni: Lázaro Calderín , Deb Chakraborty, Támas Gál,

Valentin Karasiev, Olga Shukruto, Travis Sjostrom

XC Functional Collaboration (Mexico City):

José Luis Gázquez (UAM- I), Alberto Vela (Cinvestav), Jorge Martín del Campo Ramírez (UNAM), Javier Carmona-Espíndola (UAM-I), Angel M. Albavera Mata (Cinvestav)

***DFT in Magnetic Fields Collaboration*:**

Wuming Zhu (Hangzhou Normal Univ., China)

National Energy Research Scientific Computing Center

Funding Acknowledgments:

U.S. Dept. Energy DE-SC 0002129

U.S. Nat. Science Foundation DMR 1515307

CONACYT (México)

Publications, preprints, & software at http://www.qtp.ufl.edu/ofdft

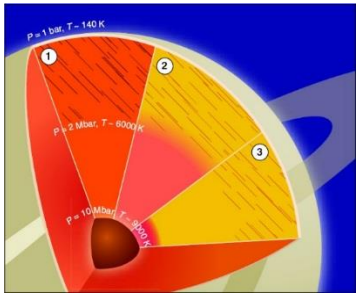
UF

Motivating physical problem & current practice -

Warm Dense Matter (WDM)

- **Challenging region *between* normal condensed matter and plasmas:**
  T < 100eV (≈1,100,000 K) *P* from 0 → thousands of GPa.
- **Inertial confinement fusion pathway; giant planet & exo-planet interiors; shock compression experiments**

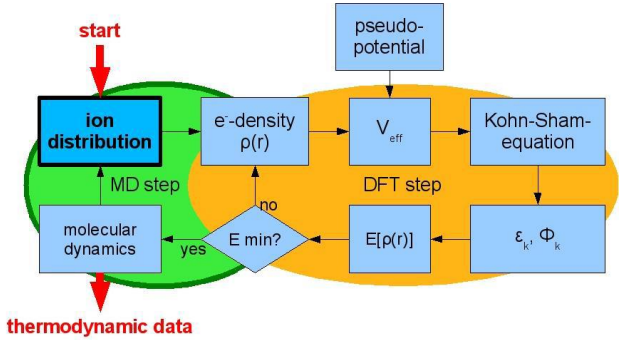
Warm Dense Matter Panel, High Energy Density Laboratory Plasma ReNew Workshop; Nov. 2009



Left: Interior of Saturn [J.J. Fortney, Science 305, 1414 (2004)]:
(1) At an age of ≈ 1.5 billion years
(2) Current Saturn according to previous H-He phase diagram
(3) Current Saturn according to newer evolutionary models

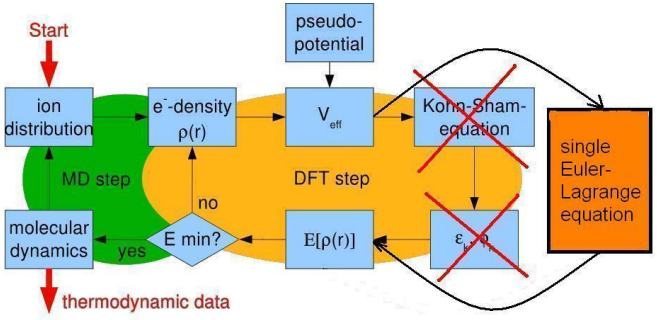
Current Practice to handle materials under such extreme conditions = ab initio Molecular Dynamics (AIMD)

- **Born-Oppenheimer MD**
- **Free-energy DFT for electronic forces (consumes vast majority of run time)**

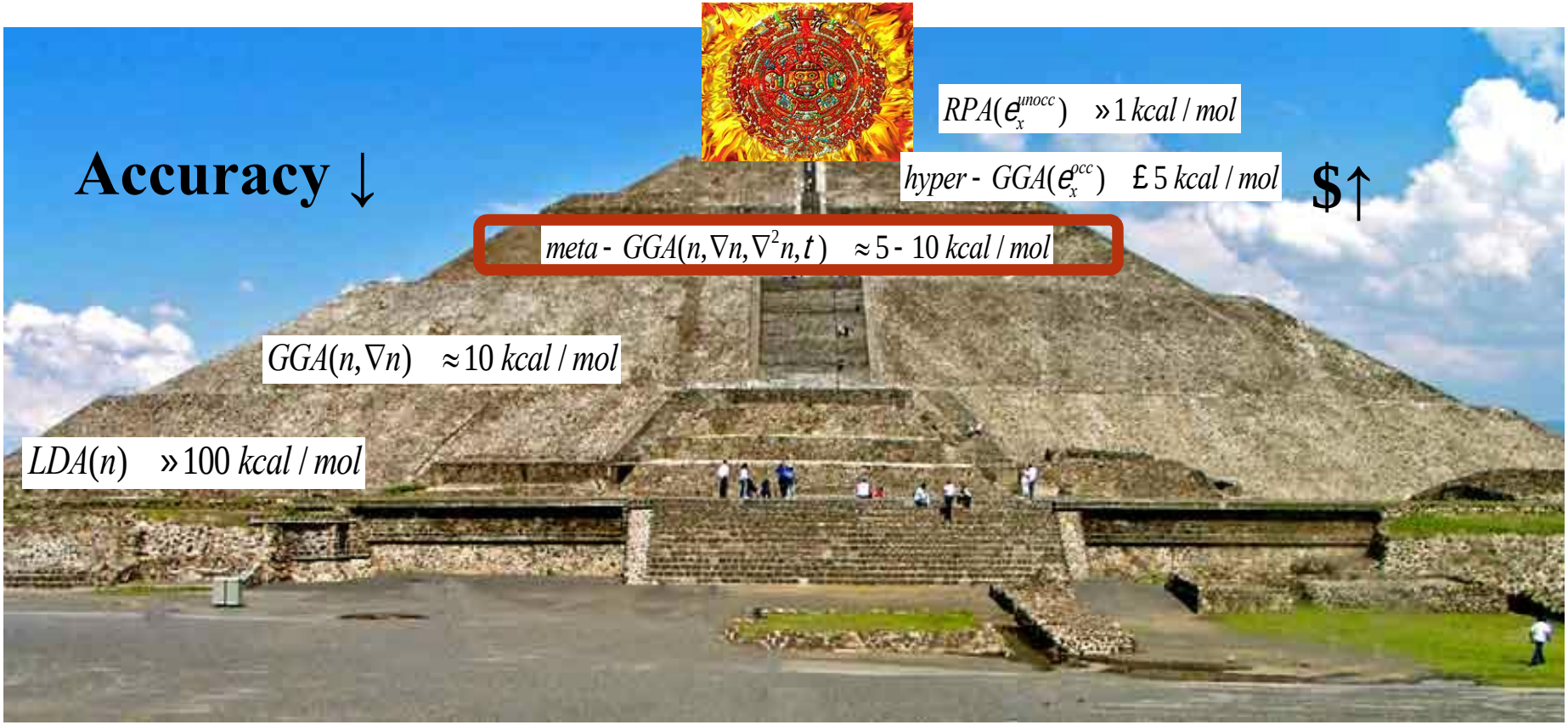


Desiderata for AIMD -

- **Accurate, computationally efficient exchange-correlation (XC) free energy functional**
- **Orbital-free DFT for linear scaling ⇒**
  - **orbital-free non-interacting KE and non-interacting entropy**
  - **orbital-free XC free energy ⇒ orbital-free XC energy (ground-state)**



Jacob's Ladder = Perdew-Schmidt pyramid (T=0 K)



$$E_{XC}[n] = \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_X(n)\, F_{XC}(n, \nabla n, \cdots) \qquad E_x^{XX}\left[\{\phi_i(\mathbf{r})\}\right] = -\frac{1}{2}\sum_{i,j}\left[\int \frac{\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'\right]$$

Borrowed from A. Vela

UF

Climbing Perdew's Pyramid

Conventional zero-temperature meta-GGA functionals -

$$E_{xc}[n] = \int d\mathbf{r}\, \varepsilon_{xc}^{ueg}(n)\, F_{xc}\left(n, \nabla n, \tau(\varphi)\right)$$

$$\tau(\varphi[n]) = \frac{1}{2}\sum_i f_i \left|\nabla \varphi_i\right|^2$$

$$T_s[n] = \int d\mathbf{r}\, t(\varphi[n])$$

KS kinetic energy density; Orbital dependence

- PKZB [Phys. Rev. Lett. **82**, 2544 (1999)]
- TPSS [Phys. Rev. Lett. **91**, 146401 (2003)]
- TM [Phys. Rev. Lett. **117**, 073001 (2016)]

$$z := \tau_W / \tau(\varphi)$$

$$\alpha := \frac{\tau(\varphi) - \tau_W}{\tau_{TF}}$$

- TPSS
- MVS [PNAS **112**, 685 (2015)]
- SCAN [Phys. Rev. Lett. **115**, 036402 (2015)]

$$w := \frac{\tau_{TF}/\tau(\varphi) - 1}{\tau_{TF}/\tau(\varphi) + 1}$$

- M06L [J. Chem. Phys. **125**, 194101 (2006)]

VT-84F (T = 0 K) as a deorbitalizer?

Try this

$$\alpha^{approx} := \frac{\tau_s^{approx} - \tau_W}{\tau_{TF}}$$

$$T_s^{GGA}[n] = c_{TF}\int dr\, n^{5/3}(\mathbf{r}) F_t\left(s(\mathbf{r})\right)$$

$$\tau_s^{approx} = c_{TF} n^{5/3}\left(F_\theta^{VT84F} + \frac{5s^2}{3}\right)$$

Quality measure (initial screening)

$$\sigma = \frac{1}{T_s}\int dr \left|\tau_s^{orb} - \tau_s^{approx}\right|; \quad \tau_s^{orb} \equiv \tau_s(\varphi)$$

J. Chem. Phys. **127**, 144109 (2007)

Evaluated post-scf on HF densities for first 18 neutral atoms

Exemplifies something basic. A good

$$T_s^{GGA}[n] = \int dr\, \tau_s^{approx}$$

doesn't guarantee a good τ_s^{approx} **(Gauge problem).**

TABLE I. Average σ values for the first 18 neutral atoms computed with several kinetic-energy density functionals. "Regularized" denotes conformance with the von Weizsäcker lower bound. Other functionals not referenced in the text also were used, including Tran and Wesolowski (TW02) [49], Lembarki and Chermette (LC94) [50], Ou-Yang and Levy (OL1 and OL2) [51] and Ernzerhof (E00) [52]. Functionals ending in "+L" were built by adding $20/9\,q$ to their original enhancement function.

Functional	Regularized?	σ
PBE2	no	1.576
VT84F	no	1.405
PBE4	no	1.272
LP	no	1.112
APBEK	no	1.028
TW02	no	1.027
LC94	no	1.027
OL2	no	1.017
OL1	no	1.016
GEA2	no	1.013
E00	no	0.996
LP+L	yes	0.827
W	yes	0.473
RDA	yes	0.382
CR	yes	0.271
MVT84F	yes	0.243
TW02+L	yes	0.239
GEA2+L	yes	0.237
MVT84F+L	yes	**0.164**
TFLreg	yes	**0.147**
PC	yes	**0.117**
CRloc	yes	**0.103**

D. Mejía Rodríguez and S.B.T.; Phys. Rev. A 96, 052512 (2017)

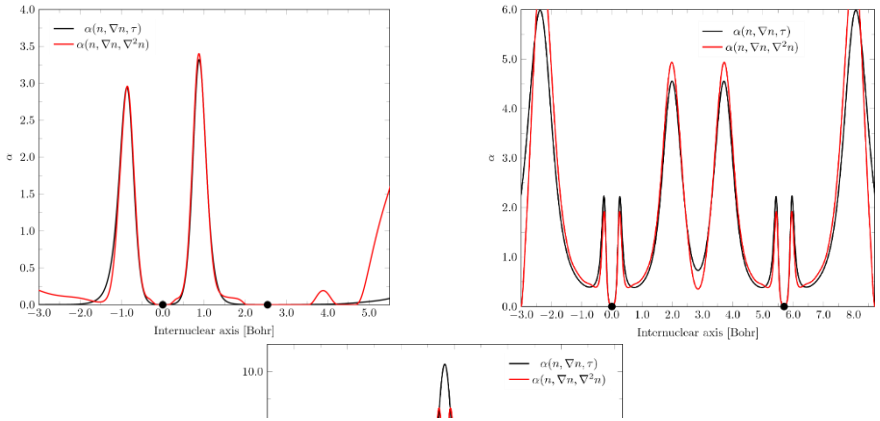
Reparametrize α directly

Quality measures

$$\delta_\alpha := \frac{1}{N_{systems}} \int d\mathbf{r}\, n(\mathbf{r}) \left| \alpha^{orb} - \alpha^{approx} \right|$$

J. Chem. Phys. **146**, 064105 (2015)

$$\delta_\alpha^{near} := \frac{4\pi}{N_{systems}} \int_0^4 dr\, r^2 n(\mathbf{r}) \left| \alpha^{orb} - \alpha^{approx} \right|$$



Again, evaluated post-scf on HF densities for first 18 neutral atoms

TABLE III. Error indicator $\Delta_\alpha + \Delta_\alpha^{near}$ values for the reoptimized mGGA$\{a,b\}$ kinetic-energy density-functional approximations.

	a	b	$\Delta_\alpha + \Delta_\alpha^{near}$
PC	0.538900	3.000000	0.712057
PCopt	1.784720	0.258304	0.649567
CRloc	−0.275000	2.895000	0.631376
TFLreg	0.000000	2.222222	0.398936
CRopt	−0.295491	2.615740	0.383805
TANH	−0.216872	2.528000	0.365022
TFLopt	−0.203519	2.513880	0.361805

D. Mejía Rodríguez and S.B.T.;
Phys. Rev. A 96, 052512 (2017)

Deorbitalize meta-GGA made very simple ("MVS")

$$E_{xc}[n] = \int d\mathbf{r}\, \varepsilon_{xc}^{HEG}(n)\, F_{xc}\left(n, \nabla n, \tau(\varphi)\right)$$

$$F_x^{MVS}(s,\alpha) = \frac{1 + 0.174\, f_x(\alpha)}{(1 + 0.0233 s^4)^{1/8}}; \qquad f_x(\alpha) = \frac{1-\alpha}{\left[(1-1.6665\alpha^2)^2 + 0.7438\alpha^4\right]^{1/4}}$$

	Original	PCopt	CRopt
Heats of formation (kcal/mol)	18.34	15.94	6.20
Bond Lengths (Å)	0.0139	0.013	0.0130
Frequencies (cm^{-1})	52.0	46.0	42.6

Surprise! Best-performing deorbitalization; superior to original.

Gratifying result: faithful deorbitalization resembles MAD of original nicely

D. Mejía Rodríguez and S.B.T.;
Phys. Rev. A 96, 052512 (2017)

Deorbitalize SCAN

$$E_{xc}[n] = \int d\mathbf{r}\, \varepsilon_{xc}^{HEG}(n)\, F_{xc}\left(n, \nabla n, \tau(\varphi)\right)$$

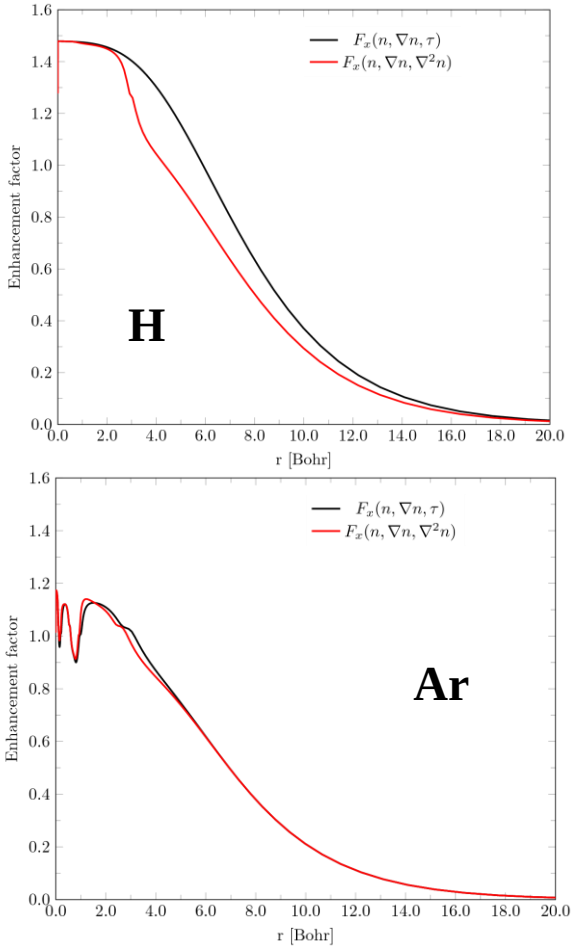
$$F_x^{scan}(s,\alpha) = \left\{ h_x^1(s,\alpha) + f_x(\alpha)\left[1.174 - h_x^1(s,\alpha)\right]\right\} g_x(s)$$

$$g_x(s) = 1 - e^{-a_1/\sqrt{s}}$$

$$f_x(\alpha) = e^{-c_{1x}\alpha/(1-\alpha)}\theta(1-\alpha) - d_x e^{c_{2x}/(1-\alpha)}\theta(\alpha - 1)$$

$h_x^1(s,\alpha)$ is an approximate resummation of the fourth-order gradient expansion for exchange

$\theta(x)$ is the Heaviside unit step function



At right: plots of F_{xc} for SCAN (black) and SCAN-L (red) for H and Ar atoms; SCAN-L done with PCopt deorbitalization

D. Mejía Rodríguez and S.B.T.;
Phys. Rev. A 96, 052512 (2017)

Original SCAN vs. SCAN-L: molecular benchmark

		SCAN	SCAN-L
Heats of formation G3 Set [kcal/mol]	**ME**	**-3.62**	**2.11**
	MAE	**5.12**	**5.67**
Bond distances T96R [Å]	**ME**	**0.0035**	**0.0073**
	MAE	**0.0089**	**0.0105**
Vibrational frequencies T82F [cm^{-1}]	**ME**	**15.3**	**-11.7**
	MAE	**31.9**	**28.7**

SCAN-L performs essentially as well as SCAN for these standard molecular tests.

Convergence of both SCF and geometry optimization are stable.

D. Mejía Rodríguez and S.B.T.;
Phys. Rev. A 96, 052512 (2017)

Original SCAN vs. SCAN-L: crystalline benchmark

		SCAN	SCAN-L
Lattice constants [Å]	**ME**	**0.011**	**0.009**
	MAE	**0.025**	**0.024**
	MARE(%)	**0.53**	**0.55**
Bulk moduli [GPa]	**ME**	**3.0**	**-3.0**
	MAE	**6.9**	**9.2**
	MARE(%)	**7.1**	**9.4**
Cohesive energies [eV/atom]	**ME**	**-0.01**	**-0.017**
	MAE	**0.24**	**0.26**
	MARE(%)	**5.93**	**6.42**
KS Band gaps [eV]	**ME**	**-1.26**	**-1.58**
	MAE	**1.26**	**1.58**

VASP with PBE PAWs

SCAN-L performs as well as SCAN for 57 solids.

SAME deorbitalization for solids *and* molecules.

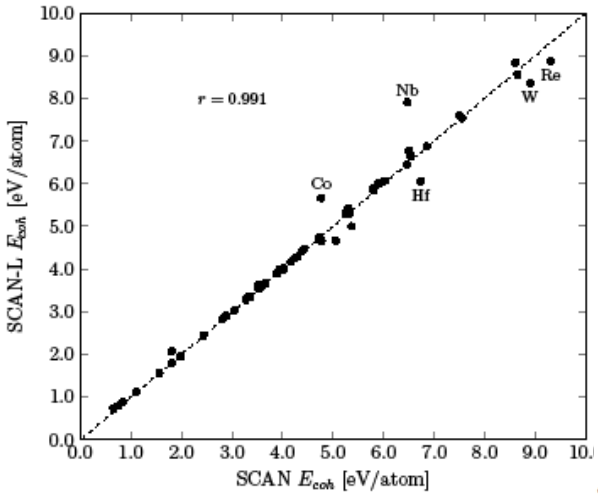
SCF convergence for SCAN-L is same or faster than SCAN

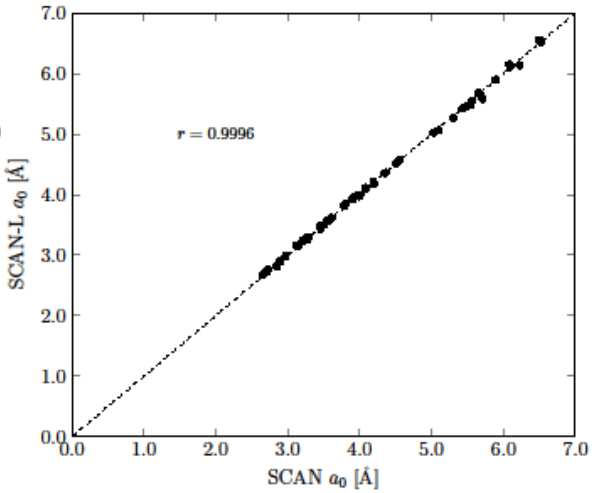
Overall SCAN-L speed in VASP is 3 times faster than SCAN.

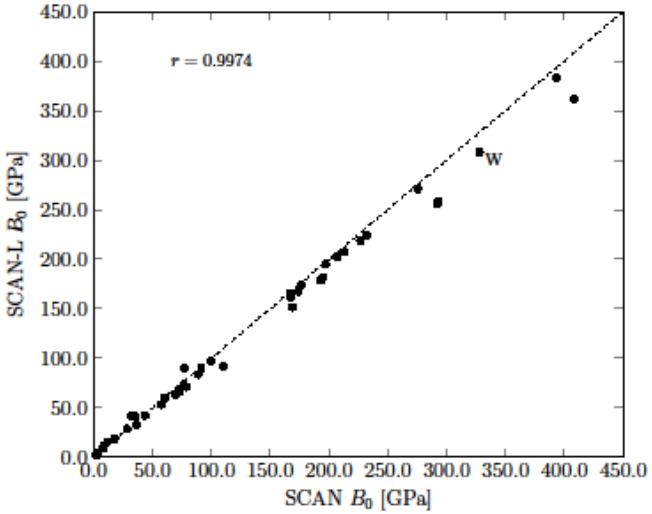
Band gap difference reflects difference between gKS (SCAN) and KS (SCAN-L)

D. Mejía Rodríguez and S.B.T.;
arXiv 1807.09216

Original SCAN vs. SCAN-L: crystalline benchmark

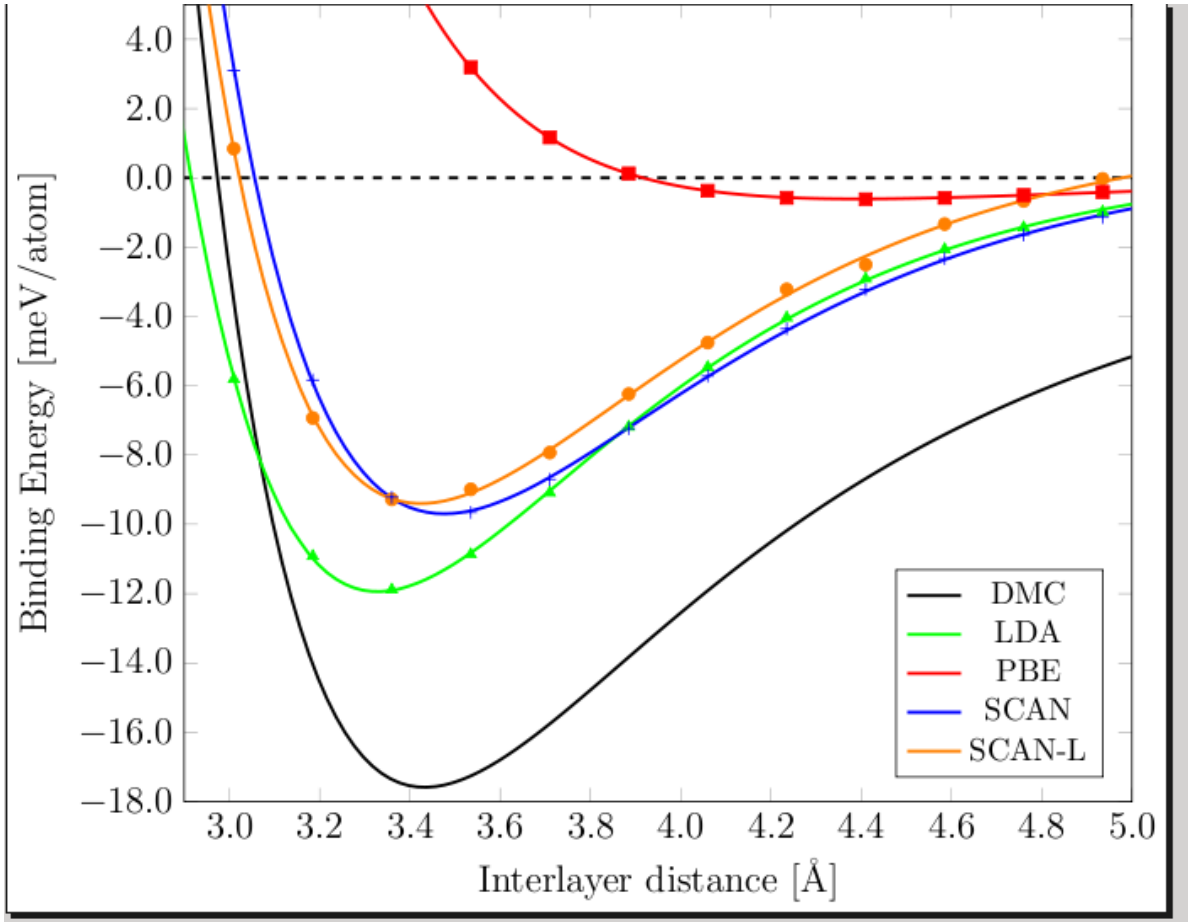






D. Mejía Rodríguez and S.B.T.;
arXiv 1807.09216

Original SCAN vs. SCAN-L: Graphene bilayer interlayer binding



D. Mejía Rodríguez and S.B.T.;
arXiv 1807.09216

DMC data: Phys. Rev. Lett. **115**, 115501 (2015)

VASP timings

TABLE VII. Comparative timings for PBE, SCAN, and SCAN-L calculations in the original and modified mGGA and GGA trunks of VASP. All times in seconds. See text for trunk labels.

XC	Trunk	Original Code	Modified Code
PBE	GGA=PE	12.38	12.85
PBE	METAGGA=PBE	36.75	37.57
SCAN	METAGGA=SCAN	61.28	–
SCAN-L	GGA=SL	–	19.32
SCAN-L	METAGGA=SCANL	–	50.72

D. Mejía Rodríguez and S.B.T.;
arXiv 1807.09216

Summary

*** SCAN-L = de-orbitalized SCAN makes modern mGGA XC functional useful for orbital-free calculations**

*** *SAME* deorbitalization for *both* solids *and* molecules**

*** SCAN-L via GGA trunk in VASP is 3 times faster than SCAN**

*** SCAN-L available in NWChem development version; will be in VASP 6.**

*** Renews motivation for studying Laplacian-dependent XC functionals (one de-orbitalized version of MVS is better than original)**

*** Finite-T version of SCAN-L coming**

Downloads - www.qtp.ufl.edu/ofdft