Addressing Accuracy and Precision in Density Functional Theory

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Accuracy and Precision

Accuracy refers to the closeness of a measured value to a standard or known value. For example, if in lab you obtain a weight measurement of 3.2 kg for a given substance, but the actual or known weight is 10 kg, then your measurement is not accurate. In this case, your measurement is not close to the known value.

Precision refers to the closeness of two or more measurements to each other. Using the example above, if you weigh a given substance five times, and get 3.2 kg each time, then your measurement is very precise. Precision is independent of accuracy. You can be very precise but inaccurate, as described above. You can also be accurate but imprecise.

For example, if on average, your measurements for a given substance are close to the known value, but the measurements are far from each other, then you have accuracy without precision.





FIG. 1. Numbers of papers when DFT is searched as a topic in Web of Knowledge (grey), B3LYP citations (blue), and PBE citations (green, on top of blue).



Independent electrons in an effective potential

$$V(\mathbf{r},\mathbf{R}) = rac{e^2}{2} rac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - rac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + rac{e^2}{2|\mathbf{r}_i - \mathbf{r}_i|}$$
 $\left[-rac{\hbar^2}{2m_e} \nabla^2 + V_{eff}(\vec{r},\mathbf{R}) \right] \phi_i(\vec{r}) = \varepsilon_i \ \phi_i(\vec{r})$

r



Hohenberg and Kohn theorem

 $[T_e + W_{eI} + W_{ee} + W_{II}] \Phi_{\nu}(\mathbf{r}|\mathbf{R}) = E_{\nu}(\mathbf{R})\Phi_{\nu}(\mathbf{r}|\mathbf{R})$

The GS density can be uses as basic variable to describe the status of a quantum many-body system.

All properties of the system are therefore functionals of the GS density.



Hohenberg and Kohn theorem

In QM potential V(r) determines the GS density n(r)

$$E_{GS}[V] = \min_{\Psi} \langle \Psi | [T_e + W_{ee} + V | \Psi \rangle$$
$$V(\mathbf{r}) \implies \Psi \implies n(\mathbf{r}) = \langle \Psi | \hat{n} | \Psi \rangle = \frac{\delta E_{GS}}{\delta V(\mathbf{r})}$$



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Performing a Legendre transform we obtain

$$F[n] = \max_{V} \left\{ E_{GS}[V] - \int V(\mathbf{r})n(\mathbf{r})d\mathbf{r} \right\}$$
$$= \min_{\Psi \to n} \langle \Psi | T_e + W_{ee} | \Psi \rangle$$
$$n(\mathbf{r}) \implies \Psi \implies V(\mathbf{r}) = -\frac{\delta F[n]}{\delta n(\mathbf{r})}$$



The GS density n(r) determines the potential V(r)

Density Functional Theory

 $[T_e + W_{eI} + W_{ee} + W_{II}] \Phi_{\nu}(\mathbf{r}|\mathbf{R}) = E_{\nu}(\mathbf{R})\Phi_{\nu}(\mathbf{r}|\mathbf{R})$

HK:
$$n(\mathbf{r}) \longrightarrow F[n] = \min_{\Psi \to n} \langle \Psi | T_e + W_{ee} | \Psi \rangle$$

F[n] depends on the GS density $n(\mathbf{r})$ (a 3D function) and $E_{GS}(\mathbf{R})$ satisfies the variational principle [Hohenberg and Kohn, 1964]

$$E_{GS}(\mathbf{R}) = \min_{n} \left\{ F[n(\mathbf{r})] + \int V_{ext}(\mathbf{r}, \mathbf{R}) n(\mathbf{r}) d\mathbf{r} \right\}$$
$$+ W_{II}(\mathbf{R})$$



HK:
$$n(\mathbf{r}) \longrightarrow F[n] = \min_{\Psi \to n} \langle \Psi | T_e + W_{ee} | \Psi \rangle$$

It is useful to introduce a ficticious system of non-interacting electrons

KS:
$$n(\mathbf{r}) \longrightarrow T_s[n] = \min_{\Psi \to n} \langle \Psi | T_e | \Psi \rangle$$

$$F[n] = T_s[n] + E_H[n] + E_{xc}[n]$$
 This defines E_{xc}

The energy becomes

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$



Self-consistent equations [Kohn-Sham, 1965]

$$V_{eff}(\mathbf{r}, \mathbf{R}) = V_{ext}(\mathbf{r}, \mathbf{R}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(\mathbf{r}, \mathbf{R})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = 2\sum_{i} |\phi_i(\mathbf{r})|^2$$



It is as simple as a Mean-field approach but it is exact ! $E_{xc}[n]$ is not known exactly \rightarrow approximations



F[n] is a very non trivial functional of n(r) ...



FIG. 1. Spherically averaged density n(r) in ground state of carbon atom as a function of distance r from nucleus.



... still simple approximations are possibles

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$



FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).



Local Density Approximation

The simplest approximation is LDA that exploits nearsightedness of the electronic matter

W. Kohn, PRL 76,3168 (1996)

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int \varepsilon_{xc}^{hom}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}$$

Analogous to the Thomas-Fermi approximation for the Kinetic Energy term but applied to the much smaller Exchange-Correlation term





FIG. 3. The alphabet soup of approximate functionals available in a code near you. Figure used with permission from Peter Elliott.

Kieron Burke, "Perspective on density functional theory" JCP 136 (2012) 150901



Here are the raw data for the DFT2015 poll.

	functional	year	like	neutral	hate	empty	points
Prime	era Divisió						
1	PBE	1996	36	18	3	19	123
2	PBE0 (PBE1PBE)	1996	34	19	2	21	119
3	B3LYP	1994	23	21	15	17	75
4	ω B97X-D	2008	22	11	4	39	73
5	B3LYP-D	2006	17	23	7	29	67
6	LDA	1980	20	14	13	29	61
7	PW91	1992	14	22	5	35	59
8	B97-D	2006	16	16	7	37	57
9	M06-2X	2008	20	10	13	33	57
10	B2PLYP	2006	16	14	6	40	56
11	CAM-B3LYP	2004	12	19	5	40	50
12	HSE	2003	12	17	3	44	50
13	BP86	1988	14	14	9	39	47
14	M06	2008	11	19	12	34	40
15	B3PW91	1993	10	17	8	41	39
16	revTPSS	2009	6	21	4	45	35
17	RPA	2008	8	13	5	50	32
18	TPSSh	2003	6	18	5	47	31
19	M06-L	2006	7	15	12	42	24
20	BLYP	1988	6	18	17	35	19



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Is the DFT description accurate ?

Is the DFT implementation precise ?



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Is the DFT description accurate ?(validation)Is the DFT implementation precise ?(verification)











Is the DFT implementation precise ?



DFT METHODS

Reproducibility in density functional theory calculations of solids

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ienna imulation													21	5			
H 0.05																	He 0.01
LI 0.06	Be 0.23											B 0.31	C 1.05	N 0.55	0 0.41	F 0.09	Ne 0.09
Na 0.72	Mg 0.54											Al 0.13	SI 0.17	P 0.86	S 0.07	CI 1.40	Ar 0.05
K 0.07	Ca 0.45	Sc 0.44	TI 0.72	V 1.03	Cr 0.79	Mn 0.54	Fe 0.63	Co 1.91	Ni 0.35	Cu 1.80	Zn 1.18	Ga 0.68	Ge 0.38	As 1.24	Se 0.65	Br 0.08	Kr 0.11
Rb 0.13	Sr 0.10	Y 0.57	Zr 0.52	Nb 0.62	Mo 2.40	Tc 1.37	Ru 0.31	Rh 0.72	Pd 0.54	Ag 0.17	Cd 3.21	In 0.33	Sn 0.08	Sb 0.44	Te 0.15	I 0.44	Xe 0.12
Cs 0.03	Ba 0.84		Hf 1.99	Та 0.43	W 0.95	Re 2.10	Os 0.78	lr 1.37	Pt 1.58	Au 0.44	Hg 0.98	TI 0.21	Pb 0.07	Bi 0.14	Po 0.56	At	Rn 0.04

b-initio

Δ (VASP, WIEN2k) = 0.4 meV/atom

			ight				A	Ε									F	A	W					ŕ		U	SP	Р				N	P	Ρ		
		exciting	FMI -ABMS/really1	FHI -AIMS//tior2	FHE -ABMS/Tight	FUDUR	FPLO/default	FPLO/T+F	FPL0/7+F+5	IPLO/TeFes CEPt ATENCA/default ATENCA/default				CONVL2/AGINIT	CPANDE/CPAN	CPAMPS/ABINIT	CPAMPRI' CPAM	JTHOR2 / ALB IN LT	PS1.18-601.1QE	PS140300/06	VAGP2821/VAGP	VIGP2852/VIGP	VASPONDES/VASP	GBP112/QE	588Y14/0E	OTFG7/CASTEP	OTFG8//CASTUP	3014555	VOLVENERE	V@2/GACAPO	TIMBAL/INP	AIWIN/WESH	HGH-NLCC/Big0FT	MBK/Operatio	ONCAPSP/ABINITY	040/638/3018)/d6
30	exciting		0.5	01	0.5	05	3.9	10	0.9	0.8	02	17	12	0.8	3.8	13	15	0.5	18	0.8	21	0.6	0.4	10	1.0	25	05	0.3	7.7	63	345	22	12	21	1.0	13
FHI	-aims/reallytight	0.5		0.5	00	0.7	3.8	0.9	11	0.8	0.5	18	13	1.0	3.8	13	1.6	0.7	1.9	10	22	0.8	0.6	11	11	2.6	0.7	0.6	2.7	63	34.6	22	13	2.0	12	1.4
	FH2-aims/tier2	01	0.5		0.5	0.5	3.9	0.9	0.9	0.8	0.2	17	12	0.8	3.8	13	15	0.5	1.8	0.8	2.0	0.6	0.4	0.9	0.9	25	0.5	0.3	7.7	63	14.5	2.2	1.2	21	0.9	13
	FH2-aims/tight	0.5	00	0.5		0.7	3.8	0.9	11	0.8	0.5	1.8	13	1.0	3.8	13	1.6	0.7	19	1.0	22	0.8	0.6	11	11	2.6	07	0.6	2.7	63	34.6	22	13	2.0	12	1.4
	FLEUR	0.5	0.7	0.5	0.7		3.6	0.8	0.8	05	0.4	14	0.9	0.9	3.5	13	15	0.5	16	0.8	19	0.7	0.6	10	1.0	2.6	0.7	0.5	7.8	63	34.2	2.0	11	19	0.8	13
ш	FPL0/default	3.9	3.8	3.9	3.8	3.6		31	3.6	3.2	3.9	29	3.4	4.0	31	41	41	3.6	3.3	3.9	2.8	3.9	4.0	40	41	5.8	40	3.9	8.9	7.2	13.6	4.9	3.7	3.2	40	41
\triangleleft	FPLO/T+F	10	0.9	0.9	0.9	0.8	31		0.8	67	0.9	1.4	1.0	13	3.4	17	19	0.9	16	1.5	19	12	10	13	13	3.1	12	10	7.9	64	14.6	24	13	1.8	13	1.6
	FPLO/T+F+S	0.9	11	0.9	11	0.8	3.6	0.8		0.9	0.9	15	11	13	3.5	17	18	0.9	16	1.3	19	12	10	14	1.4	29	11	0.9	2.7	64	13.9	23	13	18	13	1.6
	RSPt	0.8	0.8	0.8	0.8	0.6	3.2	0.7	0.9		0.8	1.3	0.9	12	3.4	15	1.6	07	16	1.2	19	10	0.9	13	13	3.0	11	0.8	7.9	65	34.0	2.2	13	1.8	11	1.4
	WIEN2k/acc	0.2	05	0.2	05	0.4	3.9	0.9	0.9	0.8		17	12	0.8	3.8	13	15	0.5	1.8	0.8	2.0	0.7	0.4	0.9	10	25	05	0.3	7.7	62	34.4	21	12	2.0	0.9	13
	wDEN2k/default	17	18	17	1.8	14	2.9	14	15	1.5	17		12	19	3.2	22	23	15	18	1.8	17	18	19	19	19	3.8	19	1.6	8.3	7.0	13.6	28	18	19	18	21
_	wIEN2k/enhanced	12	13	1.2	13	0.9	3.4	10	11	0.9	12	1.2		15	3.2	16	1.6	1.0	17	14	19	13	13	14	14	3.0	14	11	7.9	65	13.3	2.2	14	1.6	12	1.3
	GERV12/ABINIT	0.8	10	0.8	10	0.9	4.0	13	1.3	12	0.8	19	15		41	15	1.6	11	21	11	23	10	0.9	07	0.7	2.8	0.9	0.7	7.8	63	26.2	25	16	2.4	1.4	1.7
	GPANDE/GPAN	3.8	3.8	3.8	3.8	35	31	3.4	3.5	3.4	3.8	3.2	3.2	41		3.6	3.5	3.5	29	3.8	28	3.7	3.8	4.0	4.0	5.6	3.8	3.6	8.6	7.6	13.0	45	3.2	3.0	35	3.8
	GPAM09/ABINIT	13	1.3	1.3	13	13	41	17	1.7	15	1.3	22	16	15	3.6		0.6	14	22	15	2.4	1.4	13	1.6	1.6	25	1.4	13	7.9	61	34.2	2.3	19	2.3	13	1.7
	GPAM09/GPAM	15	1.6	15	16	15	41	1.9	1.8	16	15	23	1.6	1.6	3.5	06		15	22	16	25	16	14	17	17	2.7	15	14	7.9	61	34.2	25	20	23	16	1.8
\geq	JTH02/ABINIT	0.6	0.7	0.6	0.7	0.6	3.6	0.9	0.9	0.7	0.5	15	10	11	35	14	15		1.6	0.9	19	0.7	0.7	12	12	2.6	0.7	0.6	7.6	62	34.2	22	13	19	0.9	14
A	P5115831/QE	1.8	19	1.6	19	16	3.3	16	16	16	18	18	17	21	29	22	22	1.6		1.6	15	18	18	2.0	2.0	3.3	17	1.7	7.4	5.9	141	25	19	1.8	18	2.3
<u> </u>	P5110500/QE	0.8	10	0.8	10	0.8	3.9	1.3	1.3	12	0.8	1.8	14	11	3.8	15	1.6	0.9	1.6		17	10	0.8	11	12	2.2	0.8	0.7	7.7	5.9	13.3	21	15	1.9	1.2	1.6
	VASP2011/VASP	21	22	2.0	22	1.9	2.8	19	1.9	1.9	20	1.7	19	2.3	2.8	24	25	1.9	15	1.7		18	21	21	21	3.5	21	1.9	7.8	61	13.3	3.0	23	1.7	21	2.4
	VASP2012/VASP	0.5	0.8	0.6	0.8	0.7	3.9	12	1.2	10	0.7	1.8	13	1.0	3.7	14	1.6	0.7	18	1.0	18		0.7	11	11	25	0.8	0.6	7.8	63	14.5	2.2	13	21	11	15
	VASPOND015/VASP	0.4	0.6	04	06	0.6	4.0	10	1.0	0.9	0.4	19	13	0.9	3.8	13	14	07	1.8	0.8	21	0.7		11	11	25	05	0.4	80	62	14.6	22	13	2.2	10	1.4
_	GBRV12/QE	10	11	0.9	11	1.0	4.0	13	14	13	0.9	19	14	0.7	4.0	1.6	17	1.2	20	11	21	11	11		0.1	2.6	0.9	0.8	7.8	6.4	36.2	23	16	21	12	15
	GBRV14/QE	10	11	0.9	11	1.0	41	13	1.4	13	10	19	14	0.7	4.0	16	17	12	2.0	1.2	21	11	11	01		2.6	0.9	8.0	7.8	63	26.1	23	1.6	21	12	15
۵.	OTFG7/CASTEP	25	2.6	25	2.6	2.6	5.8	31	29	3.0	25	3.8	3.0	2.8	5.6	25	2.7	2.6	3.5	2.2	35	25	25	2.6	2.6		2.2	2.4	68	5.7	14.8	2.7	2.9	3.4	2.3	2.6
85	OTFG8/CASTEP	05	0.7	0.5	0.7	0.7	4.0	12	11	11	0.5	19	14	0.9	3.8	1.4	15	0.7	1.7	0.8	21	0.8	0.5	0.9	0.9	2.2		0.5	7.6	5.6	34.7	18	13	2.0	0.8	1.0
Š	SSSP/QE	0.3	0.6	03	0.6	05	3.9	10	0.9	0.8	0.3	1.6	11	0.7	3.6	13	1.4	0.5	17	0.7	19	0.6	0.4	0.8	0.8	2.4	05		2.7	62	34.6	21	12	2.0	0.9	1.2
	V6b/CASTEP	7.7	7.7	7.7	7.7	7.8	8.9	7.9	7.7	7.9	7.7	8.3	7.9	7.8	8.6	7.9	7.9	7.6	7.4	7.7	7.8	7.8	8.0	7.8	7.8	68	7.6	7.7		11.0	13.5	85	5.9	8.2	7.7	7.6
	V6b2/DACAPO	63	63	63	63	63	7.2	64	64	65	62	7,0	65	63	7.6	61	61	62	5.9	5.9	61	63	62	64	63	5.7	5.6	62	11.0		28.4	62	60	6.4	64	6.5
_	FHI/ABINIT	34.5	34.6	14.5	34.6	34.2	13.6	14.6	119	140	34.4	13.6	13.3	16.2	13.0	14.2	34.2	14.2	141	13.3	13.3	54.5	34.6	16.2	36.1	34.8	14.7	34.6	13.5	18.4		14.8	10.4	13.6	14.1	141
0	HON/ABINIT	2.2	2.2	2.2	22	2.0	4.9	2.4	2.3	2.2	21	2.8	22	25	45	2.3	25	2.2	25	2.1	3.0	22	22	2.3	23	2.7	1.8	21	85	62	14.8		0.8	2.6	1.7	2.0
8	HOM-NLCC/BigOFT	12	1.3	1.2	13	11	37	13	1.3	13	12	18	14	1.6	32	1.9	2.0	1.3	19	15	2.3	13	13	16	1.6	2.9	13	12	5.9	60	30.4	08		19	1.2	15
ž	MEK/OpenMX	21	2.0	21	2.0	1.9	3.2	1.8	1.8	1.8	20	19	1.6	2.4	3.0	2.3	23	1.9	1.8	1.9	17	21	2.2	2.1	21	3.4	2.0	2.0	8.2	64	13.6	2.6	19		1.9	2.2
	ONCUPSE/ABINIT	10	1.2	0.9	12	0.8	40	1.3	1.3	11	0.9	1.8	12	1.4	35	13	1.6	0.9	1.8	1.2	21	11	1.0	1.2	12	2.3	0.8	0.9	7.7	64	141	17	12	19		11
	ONCUPSP(SGSS)/QE	1.3	14	13	14	13	41	16	1.6	14	13	21	13	17	3.8	17	1.8	14	23	1.6	2.4	15	14	15	15	2.6	1.0	12	7.6	65	141	20	15	2.2	11	

≈ 0 ≈ 1	.01 Å GPa	exciting	FHI-aims/tier2	FLEUR	FPL0/T+F+S	RSPt	WIEN2k/acc	average < < >>
	exciting		0.1	0.5	0.9	0.8	0.2	0.5
	FHI-aims/tier2	0.1		0.5	0.9	0.8	0.2	0.5
ш	FLEUR	0.5	0.5		0.8	0.6	0.4	0.6
\triangleleft	FPL0/T+F+s	0.9	0.9	0.8		0.9	0.9	0.9
	RSPt	0.8	0.8	0.6	0.9		0.8	0.8
	WIEN2k/acc	0.2	0.2	0.4	0.9	0.8		0.5

		exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc	average < A>
	exciting		0.1	0.5	0.9	0.8	0.2	0.5
	FHI-aims/tier2	0.1		0.5	0.9	0.8	0.2	0.5
щ	FLEUR	0.5	0.5		0.8	0.6	0.4	0.6
\triangleleft	FPL0/T+F+s	0.9	0.9	0.8		0.9	0.9	0.9
	RSPt	0.8	0.8	0.6	0.9		0.8	0.8
_	WIEN2k/acc	0.2	0.2	0.4	0.9	0.8		0.5
	GBRV12/ABINIT	0.8	0.8	0.9	1.3	1.2	0.8	1.0
	GPAW09/ABINIT	1.3	13	13	1.7	1.5	1.3	1.4
\leq	GPAW09/GPAW	1.5	1.5	1.5	1.8	1.6	1.5	1.6
A	JTH02/ABINIT	0.6	0.6	0.6	0.9	0.7	0.5	0.6
-	PSlib100/QE	0.8	0.8	0.8	1.3	1.2	0.8	1.0
	VASPGW2015/VASP	0.4	0.4	0.6	1.0	0.9	0.4	0.6

	$\langle \Delta \rangle$ vs AE
Vdb/CASTEP	7.7
OTFG7/CASTEP	2.7
OTFG8/CASTEP	0.7
GPAW06/GPAW	3.6
GPAW09/GPAW	1.6
PSlib031/QE	1.7
PSlib100/QE	1.0
VASP2011/VASP	2.0
VASP2012/VASP	0.8
VASPGW2015/VASP	0.6



Is the DFT description accurate ?



Jacob's ladder of Density Functional Theory

Chemical Accuracy



Hartree World

FIGURE 1. Jacob's ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational resources. However, at present their safety can be guaranteed only on the two lowest rungs.



Jacob's ladder of Density Functional Theory LDA and LSDA

GGA : PW91, PBE, revPBE, RPBE, BLYP

META-GGA: PKZB, TPSS,

SIC, DFT+U, Hybrids

Van der Waals functionals





E	Elemental Crystal Structures: GGA pseudopotential																
H	1						m	etho	bc		exp	perim	ental	ly fou	ind to	be f	cc
				—E	bcc -	E _{fc}	c				exp	Derim	ental	IY TOU	ind to	> be b	cc
0.13 0.11 0.11	2.19 0.04 0.50	-		(k	J/mol	e)						В 34.77	-19.71 -6.00	-21.12	10.24	-4.53	
Na 0.12 0.05 0.05	Mg 1.37 0.50 0.50					VASP SGTI Saunde	-PAW E data rs et al.				*	Al 9.21 10.08 10.08	Si -1.89 -4.00 -4.00	P -16.04 7.95	S -17.65	Cl -4.46	
K 0.04 -0.05 -0.05	Ca 1.64 1.41 0.93	Sc 5.80 -3.02	Ti 4.79 0.48	V -23.95 -7.50 -15.30	Cr -36.76 -6.13 -9.19	Mn 7.41 0.78 1.80	Fe -8.45 -7.97	Co 836 1.71 4.20	Ni 9.23 7.99 7.49	Cu. 2.84 4.02 4.02	Zn 5.94 -0.08 6.03	Ga 1.48 0.70 0.70	Ge 0.70 -1.90 -1.90	As -10.71	Se -14.67	Br -2.85	
Rb 0.08 -0.20 -0.20	Sr 0.43 1.33 0.75	Y 10.02 1.19	Zr 3.61 -0.29	Nb -31.20 -13.50 -22.00	Mo -38.74 -15.20 -28.00	Tc 19.04 8.00 8.00	Ru 48.93 9.00 14.00	Rh 32,39 19,00 19,00	Pd 3.74 10.50 10.50	Ag 2.27 3.40 3.40	Cd 4.90	In 1.02 0.64 0.65	Sn 0.99 -1.11 0.25	Sb -8.96	Te -11.19	I -1.26	
Cs 0.10 -0.50 -0.50	Ba -1.62 -1.80 -1.80		Hf 10.14 2.38 -4.14	Ta -23.75 -16.00 -26.50	W -45.03 -19.30 -33.00	Re 24.87 6.00 18.20	Os 70.92 14.50 30.50	Ir 59.39 32.00 32.00	Pt 7.85 13.00 15.00	Au 1.90 4.25 4.25	Hg -1.02	Tl -1.40 -0.09 0.07	Pb 4.06 2.40 2.40	Bi -4.53 1.40	Po	At	
		La 12.22	Ce 22.40	Pr 11.55	Nd 11.99	Pm 12.55	Sm 12.88	Eu -1.61	Gd 13.11	Tb 12.97	Dy 12.73	Ho 12.36	Er 11.86	Tm	Yb	Lu 9.91	
Fr	Ra	Ac 12.56	Th 13.95	Pa 17.09	U -10.36	Np -23.17	Pu 11.73	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

data taken from:

Y. Wang *a S. Curtarolo, et al. Ab Initio Lattice Stability in Comparison with CALPHAD Lattice Stability, Computer Coupling of Phase Diagrams and Thermochemistry (Calphad) Vol. 28, Issue 1, March 2004, Pages 79-90.

El	Elemental Crystal Structures: GGA pseudopotential															
	1						me	tho	d		expe	erime	ntally	four	nd to	be hcp
H -0.01	Ehcp - Efcc											erime	ntally	four	nd to	be fcc
Li 0.19 -0.05 -0.05	Be -7.91 -6.35	5		(1	cJ/mol	le)						B -78.73	C -6.18 -3.00	N -34.15	0 1.00	F -14.64
Na 0.06 -0.05 -0.05	Mg -1.22 -2.60 -2.60	ŧ				VASP SGTI Saunde	-PAW E data rs et al.				*	Al 2.85 5.48 5.48	Si -3.26 -1.80 -1.80	P -3.77	S -43.63	Cl -16.81
K 0.26 0.00	Ca 0.31 0.50 0.50	Sc -4.48 -5.00	Ti -5.51 -6.00 -6.00	V 0.53 -3.50 4.80	Cr 0.91 -2.85 -1.82	Mn -3.01 -1.00 -1.00	Fe -7.76 -2.24	Co -1.95 -0.43 -0.43	Ni 2.22 2.89 1.50	Cu 0.52 0.60 0.60	Zn -0.79 -2.97	Ga 0.69 0.70 0.70	Ge -0.28 -1.00 -1.00	As -4.83	Se -35.43	Br 3.00
Rb -0.01 0.00	Sr 0.38 0.25 0.25	Y -2.13 -6.00	Zr -3.69 -7.60 -7.60	Nb -3.08 -3.50 -5.00	Mo 1.14 -3.65 -5.00	Tc -6.53 -10.00 -10.00	Ru -10.79 -12.50 -12.50	Rh 3.26 3.00 3.00	Pd 2.50 2.00 2.00	Ag 0.29 0.30 0.30	Cd -1.00 -0.89	In 0.35 0.37 0.65	Sn -0.50 -1.61 -0.25	Sb -3.94	Te 23.40	I 0.99
Cs -0.06 0.00	Ba -0.40 0.20 0.20		Hf -6.82 -10.00 -10.00	Ta 3.06 -4.00 -6.50	W -1.79 -4.55 -6.00	Re -6.26 -11.00 -11.00	Os -13.26 -13.00 -13.00	Ir 6.55 4.00 4.00	Pt 5.02 2.50 2.50	Au 0.08 0.24 0.55	Hg -1.51 -2.07	Tl -1.80 -0.31 -0.31	Pb 1.80 0.30 0.30	Bi -4.03	Po	At
		La 2.63	Ce 8.50	Pr 2.07	Nd 1.94	Pm 1.77	Sm 1.53	Eu 0.24	Gd 0.77	Tb 0.24	Dy -0.41	Ho -1.18	Er -1.97	Tm	Yb	Lu -3.85
Fr	Ra	Ac 0.93	Th 4.00	Pa 0.49	U -15.79	Np -14.01	Pu 0.69	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

data taken from:

Y. Wang,*a S. Curtarolo, at al. Ab Initio Lattice Stability in Comparison with CALPHAD Lattice Stability, Computer Coupling of Phase Diagram and Thermochemistry (Calphad) Vol. 28, Issue 1, March 2004, Pages 79-90. In standard DFT an electron interacts with the effective potential generated by all the electrons (including itself)

$$H = \sum_{i} H_{i} = \sum_{i=1}^{N_{e}} \nabla_{i}^{2} + \sum_{i=1}^{N_{e}} V_{nuclear}(r_{i}) + \sum_{i=1}^{N_{e}} V_{effective}(r_{i})$$

 $\rho(r)$



Redox Reactions can be n	nore Pro	blematic
FePO ₄ + Li -> LiFePO ₄	GGA 2.8 eV	Exp 3.5 eV
MnO ₂ + Li -> LiMn ₂ O ₄	3.6 eV	4.1 eV
V ₂ (PO ₄) ₃ + Li -> LiV ₂ (PO ₄) ₃	3.3 eV	4.6 eV

All these reactions involve the transfer of an electron from a delocalized state in Li metal to a localized state in the transition metal oxide (phosphate)



van der Waals

van der Waals interaction is relatively weak but widespread in nature. An important source of stability for molecular solids and physisorption of molecules on surfaces.



It is due to truly non-local correlation effects. It is contained in the true XC functional but LDA/GGA/MetaGGA and Hybrids do not describe it properly.





Jacob's ladder of Density Functional Theory

LDA and LSDA simple and well defined. good geometries, overbinding

GGA : PW91, PBE, revPBE, RPBE, BLYP many options, improved energetics, good geometries

META-GGA: PKZB, TPSS, more complicated, not very much used, with potential

SIC, DFT+U, Hybrids address the self-interaction error with some drawback

Van der Waals functionals truly non local, very active field



REPORT

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THEORETICAL CHEMISTRY

Density functional theory is straying from the path toward the exact functional

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The theorems at the core of density functional theory (DFT) state that the energy of a many-electron system in its ground state is fully defined by its electron density distribution. This connection is made via the exact functional for the energy, which minimizes at the exact density. For years, DFT development focused on energies, implicitly assuming that functionals producing better energies become better approximations of the exact functional. We examined the other side of the coin: the energy-minimizing electron densities for atomic species, as produced by 128 historical and modern DFT functionals. We found that these densities became closer to the exact ones, reflecting theoretical advances, until the early 2000s, when this trend was reversed by unconstrained functionals sacrificing physical rigor for the flexibility of empirical fitting.



Is density functional theory straying from the path toward the exact functional ?





Method	Rung	Year	Max NE
CCSD	Ab initio		0.000
MP4sdq	Ab initio		0.246
MP3	Ab initio		0.967
MP2	Ab initio		1.514
mPW3PBE	hGGA	1998	1.778
APFD	hGGA	2012	1.813
B3PW91	hGGA	1993	1.816
PBEO	hGGA	1999	1.818
B98	hGGA	1998	1.826
BHHLYP	hGGA	1993	1.851
B97-3	hGGA	2005	1.883
mPW1PBE	hGGA	1998	1.910
B3P86	hGGA	1993	1.937
O3LYP	hGGA	2001	1.947
PBE1KCIS	hGGA	2005	1.954
mPW1PW91	hGGA	1998	1.955
B97-1	hGGA	1998	1.962
HSE06	hGGA	2006	1.982
PBEh1PBE	hGGA	1998	1.983
B97-2	hGGA	2001	2.018
B1B95	hGGA	1996	2.033
TPSS	mGGA	2003	2.042
TPSSh	hGGA	2003	2.045
TPSSm	mGGA	2007	2.077
X3LYP	hGGA	2005	2.084
SCAN	mGGA	2015	2.107
B3LYP	hGGA	1993	2.123





Method	Rung	Year	Max NE
Χα*	LDA	1974	3.777
SP86	GGA	1986	3.821
M06-L	mGGA	2006	3.974
SVWN1RPA	LDA	1980	3.977
SPBE	GGA	1997	3.978
SVWN	LDA	1980	3.984
SPZ81	LDA	1981	3.985
SPW91	GGA	1991	3.989
M06-2X	hGGA	2006	4.027
SOP	GGA	1997	4.182
SLYP	GGA	1988	4.429
M08-SO	hGGA	2008	4.676
SLATER*	LDA	1974	4.864
M08-HX	hGGA	2008	4.880
SOGGA11	GGA	2011	4.971
M06	hGGA	2006	5.420
M06-HF	hGGA	2006	6.125
N12	GGA	2012	6.709
N12-SX	hGGA	2012	6.970
M05	hGGA	2005	7.652
MN12-L	mGGA	2012	8.995
M11	hGGA	2011	10.191
MN12-SX	hGGA	2012	13.005
M11-L	mGGA	2011	15.316

 $\alpha = 0.7$ for X α and $\alpha = 2/3$ for SLATER (see supplementary materials for references).



SUMMARY

- DFT as implemented in a number of popular codes is reproducible and precise, at least for the most basic properties. *More and continuous work is needed to <u>verify</u> the correct implementation of more properties on more systems..*

- The accuracy of DFT approximations has improved over time thanks to the incorporation in the functionals of physically motivated ingredients and extensive testing. *More and continuous work is needed to <u>validate</u> proposed functionals on as diverse physical situations and known constraints as possible...*



