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A guide to exchange-correlation functionals

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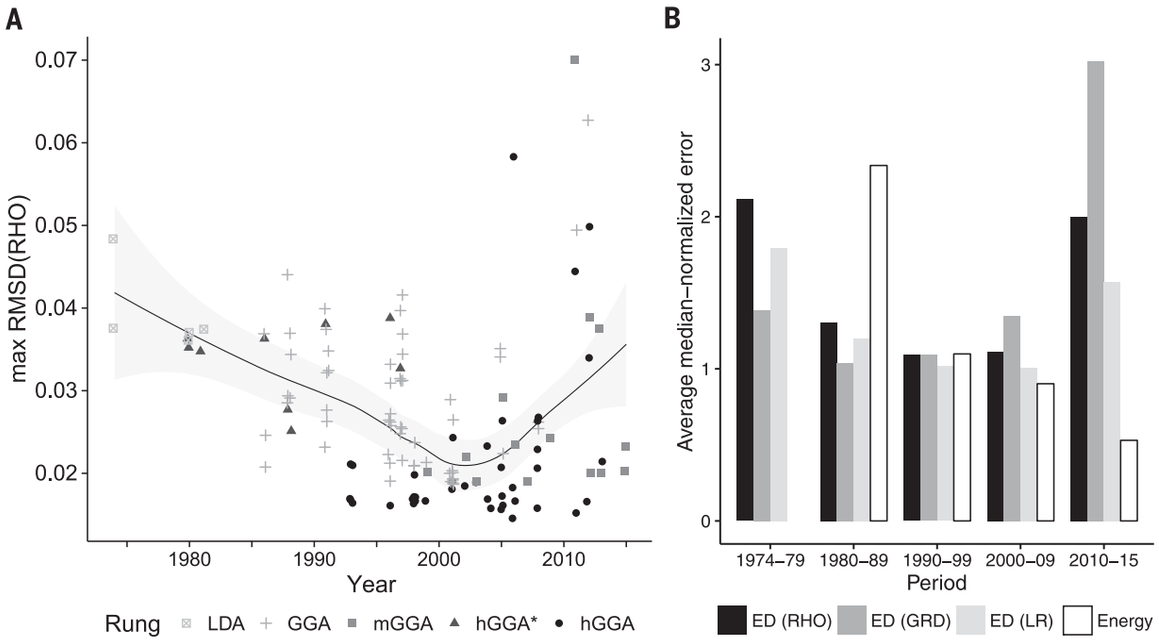
CASTEP Training Workshop 2019

Exchange-correlation functionals: A zoo



Science **355,** 49

Table 1. The L1 methods (yielding the best densities), their rungs, years, and normalized errors (NE).

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
PBE0	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

Table 2. The L2 methods (yielding the worst densities), their rungs, years, and normalized errors (NE).

Method	Rung	Year	Max NE
Xα*	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

*α = 0.7 for Xα and α = 2/3 for SLATER (see supplementary materials for references).

Results for the 2018 edition of the Annual DFT Popularity Poll: Primera Divisió

	functional	like		neutral		hate		blanc		none		#votes		points	average
1	PBE	26	55.3 %	9	19.1 %	3	6.4 %	3	6.4 %	6	12.8 %	41	87.2 %	84	1.79
2	PBE0	25	53.2 %	8	17.0 %	4	8.5 %	4	8.5 %	6	12.8 %	41	87.2 %	79	1.68
3	PBE-D	21	44.7 %	7	14.9 %	5	10.6 %	6	12.8 %	8	17.0 %	39	83.0 %	65	1.38
4	wB97X-D	19	40.4 %	7	14.9 %	4	8.5 %	13	27.7 %	4	8.5 %	43	91.5 %	60	1.28
5	B3LYP	17	36.2 %	9	19.1 %	14	29.8 %	4	8.5 %	3	6.4 %	44	93.6 %	46	0.98
6	CAM-B3LYP	14	29.8 %	9	19.1 %	6	12.8 %	12	25.5 %	6	12.8 %	41	87.2 %	45	0.96
7	B3LYP-D	13	27.7 %	9	19.1 %	9	19.1 %	10	21.3 %	6	12.8 %	41	87.2 %	39	0.83
8	B2PLYP	11	23.4 %	11	23.4 %	6	12.8 %	12	25.5 %	7	14.9 %	40	85.1 %	38	0.81
9	wB97X-V	11	23.4 %	6	12.8 %	3	6.4 %	18	38.3 %	9	19.1 %	38	80.9 %	36	0.77
10	HSE	9	19.1 %	14	29.8 %	5	10.6 %	11	23.4 %	8	17.0 %	39	83.0 %	36	0.77
11	PW91	9	19.1 %	15	31.9 %	7	14.9 %	8	17.0 %	8	17.0 %	39	83.0 %	35	0.74
12	B97-D	10	21.3 %	8	17.0 %	4	8.5 %	18	38.3 %	7	14.9 %	40	85.1 %	34	0.72
13	M06-2X	13	27.7 %	5	10.6 %	13	27.7 %	9	19.1 %	7	14.9 %	40	85.1 %	31	0.66
14	revPBE	8	17.0 %	10	21.3 %	5	10.6 %	14	29.8 %	10	21.3 %	37	78.7 %	29	0.62
15	TPSSh	8	17.0 %	9	19.1 %	5	10.6 %	16	34.0 %	9	19.1 %	38	80.9 %	28	0.60
16	PWPB95-D3	8	17.0 %	7	14.9 %	5	10.6 %	18	38.3 %	9	19.1 %	38	80.9 %	26	0.55
17	wB97M-V	7	14.9 %	8	17.0 %	3	6.4 %	18	38.3 %	11	23.4 %	36	76.6 %	26	0.55
18	LC-wPBE	7	14.9 %	9	19.1 %	5	10.6 %	16	34.0 %	10	21.3 %	37	78.7 %	25	0.53
19	BP86	6	12.8 %	9	19.1 %	8	17.0 %	14	29.8 %	10	21.3 %	37	78.7 %	19	0.40
20	B97M-V	4	8.5 %	9	19.1 %	4	8.5 %	21	44.7 %	9	19.1 %	38	80.9 %	17	0.36

total number of participants: 47

http://www.marcelswart.eu/dft-poll

Ab initio?

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Density Functional Theory

Many-body Schrödinger equation (the "truth"):

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

Hohenberg-Kohn theorems

Mapping from a many-body problem to a one-body problem

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \rightarrow n(\mathbf{r})$$

$$E[n] = F[n] + \int \mathrm{d}\mathbf{r}\ V(\mathbf{r})n(\mathbf{r}) = T[n] + U[n] + \int \mathrm{d}\mathbf{r}\ V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r})$$

Kohn-Sham formulation

Model the density with non-interacting single-electron orbitals

$$E[n] = -\frac{1}{2}\sum_{i=1}^{N} \nabla^2\psi_i + \frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\ \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\mathrm{xc}}[n] + \int \mathrm{d}\mathbf{r}\ V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r}) \qquad n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$$

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Density Functional Theory

Kohn-Sham formulation

$$E[n] = -\frac{1}{2}\sum_{i=1}^{N}\nabla^2\psi_i + \frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int \mathrm{d}\mathbf{r}\; V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r}) + E_{\mathrm{xc}}[n] \qquad n(\mathbf{r}) = \sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2$$

Kinetic energy of the non-interacting particles

$$T_s[n] = -\frac{1}{2}\sum_{i=1}^{N}\nabla^2\psi_i \quad \text{vs.} \quad T[n]$$

Hartree-term: Coulombic interaction of electrons

$$E_H[n] = \frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad \text{vs.} \quad U[n]$$

Exchange-correlation functional has to model:

- kinetic energy of the many-body system
- non-Coulombic interactions

$$E_{\mathrm{xc}}[n] = \frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\; n(\mathbf{r})\frac{n(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

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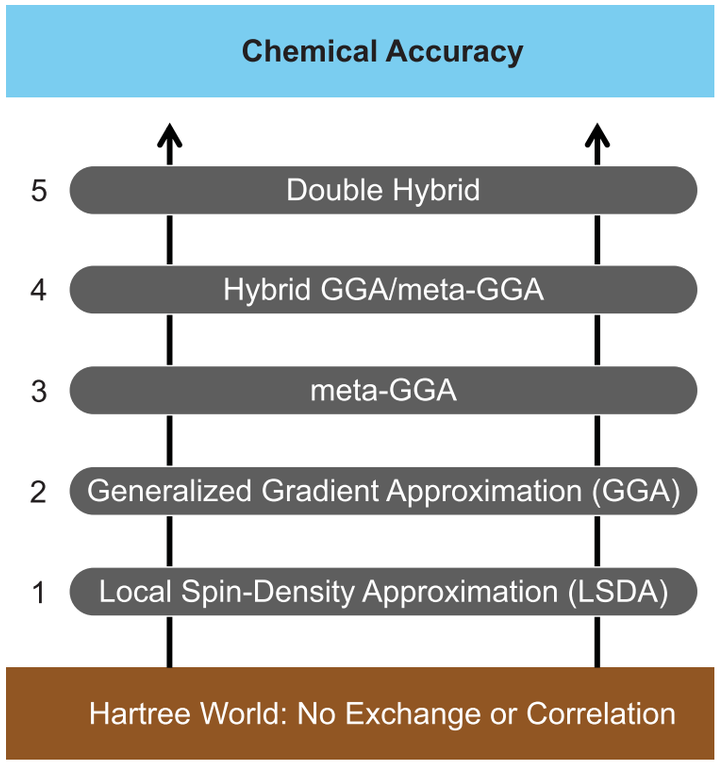
Exchange-correlation functionals

- The form of the exchange-correlation functional is unknown
- There exist a series of approximations: “Jacob’s ladder” to chemical accuracy
- Chemical accuracy: thermochemical energetics (1 kcal/mol error in formation energies), molecular geometries
- Errors in DFT can be attributed to the limitation of XC functionals
  - Self-interaction error (electron self-repulsion)
  - Derivative discontinuity
  - Non-local correlation - weak interactions



from N Mardirossian and M Head Gordon, Mol. Phys. **115** 2315

$$E_H[n] = \frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$E(N+\delta) = (1-\delta)E(N) + \delta E(N+1)$$

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Exchange-correlation functionals

(m)GGA + exact exchange + MP2 correlation

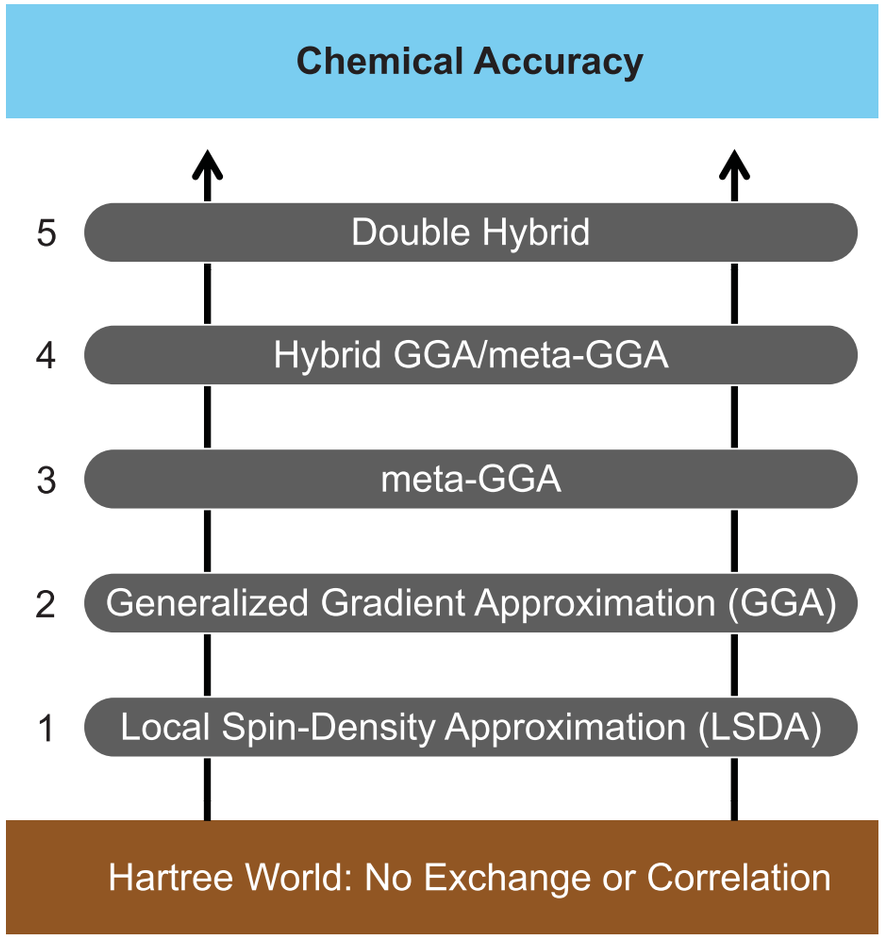
(m)GGA + exact exchange

semi-local functionals

$$E_{\mathrm{xc}} = \int \mathrm{d}\mathbf{r}\ \varepsilon_{\mathrm{mGGA}}(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r}))n(\mathbf{r})$$

$$E_{\mathrm{xc}} = \int \mathrm{d}\mathbf{r}\ \varepsilon_{\mathrm{GGA}}(n(\mathbf{r}), \nabla n(\mathbf{r}))n(\mathbf{r})$$

$$E_{\mathrm{xc}} = \int \mathrm{d}\mathbf{r}\ \varepsilon_{\mathrm{LDA}}(n(\mathbf{r}))n(\mathbf{r})$$



from N Mardirossian and M Head Gordon, Mol. Phys. **115** 2315

$\varepsilon_{\mathrm{LDA}}, \varepsilon_{\mathrm{GGA}}$ and $\varepsilon_{\mathrm{mGGA}}$ are *unknown*, need fitting!

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Generalities

- All XC functionals are approximations
  - DFT (the theory) is exact
  - Reports of ‘Failures of DFT’ are actually reports of the failure of the XC functional (approximation)
- No functional (so far) is accurate for all properties of interest
  - No matter what functional is invented, someone will always find a case where it fails
- Any functional can be applied to any electronic structure problem
  - But they have *known* limitations
  - It is still ab initio, but we use experience, benchmarks and intuition to decide which ones to use

Local Density Approximation

$$E_{\mathrm{xc}} = \int \mathrm{d}\mathbf{r}\ \varepsilon_{\mathrm{LDA}}(n(\mathbf{r}))n(\mathbf{r})$$

Typical errors:

- Binding energies too large
- Bonds and lattice parameters too small
- Incorrect order of phase stability
- Error in energetics in magnetic materials

TABLE IV. Deviation of enthalpies calculated by DFT methods with experiment.[a]

	Deviation (Expt.-Theory)						
Molecule	LDA	BLYP	BP86	BPW91	B3LYP	B3P86	B3PW91
G2-1 test set							
LiH	3.3	0.1	0.5	−4.6	0.4	1.2	−3.3
BeH	11.2	7.3	8.5	6.5	8.2	10.0	7.4
CH	9.9	1.8	4.1	−0.1	1.7	3.9	0.0
$CH_2(^3B_1)$	24.1	0.0	8.5	2.8	2.1	10.3	4.2
$CH_2(^1A_1)$	20.7	−0.6	4.2	−3.7	0.2	4.9	−2.7
CH_3	35.2	0.4	10.4	0.3	3.3	13.1	2.9
CH_4	46.8	−2.3	10.4	−3.4	1.6	14.1	0.2
NH	13.7	6.0	8.6	3.8	4.6	7.1	2.5
NH_2	29.7	8.0	13.5	4.3	6.5	11.9	3.0
NH_3	44.3	4.3	13.3	0.3	3.5	12.4	−0.4
OH	19.5	3.4	6.6	2.0	1.8	5.1	0.4
OH_2	37.3	0.6	7.8	−0.9	−1.3	5.8	−3.1
FH	22.9	0.4	4.1	−0.2	−1.6	2.2	−2.3

L. A. Curtiss *et al*, *JCP* **106**, 1063

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LDA parameterisations

$$E_{\mathrm{xc}} = \int \mathrm{d}\mathbf{r}\ \varepsilon_{\mathrm{LDA}}(n(\mathbf{r}))n(\mathbf{r})$$

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XC_FUNCTIONAL : LDA
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$\varepsilon_{\mathrm{LDA,x}} \propto n^{1/3}$

- Exchange: Slater exchange
- Correlation: parameterisations based on accurate calculations of the Homogenous Electron Gas
  - Vosko-Wilk-Nusair 5 (VWN5): Can. J. Phys. 58, 1200 (1980)
  - Perdew-Zunger: PRB 23, 5048 (1981)
  - Perdew-Wang: PRB 45, 13244 (1992)
  - VWN3: Can. J. Phys. 58, 1200 (1980)

Generalised Gradient Approximations

$$E_{\mathrm{xc}} = \int \mathrm{d}\mathbf{r}\ \varepsilon_{\mathrm{GGA}}(n(\mathbf{r}), \nabla n(\mathbf{r}))n(\mathbf{r})$$

- More flexible functional form
- Semi-local: information about nearby regions via the gradient
- Not very successful before 1996 (PBE: Generalised Gradient Approximation Made Simple)
- Theoretical limits and constraints explicitly built in
- Modifies LDA exchange and correlations using “enhancement factors”

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Generalised Gradient Approximations

	Lattice constants (Å)				Binding energies (eV / atom)			
Solids	LSDA	PBE	PBEsol	Expt.	LSDA	PBE	PBEsol	Expt.
Li	3.362	3.431	3.426	3.453	1.810	1.605	1.677	1.658
Na	4.051	4.198	4.170	4.214	1.256	1.082	1.154	1.119
Ca	5.332	5.518	5.448	5.553	2.220	1.917	2.117	1.86
Sr	5.791	6.027	5.916	6.045	1.893	1.609	1.808	1.73
Ba	4.770	5.030	4.894	4.995	2.246	1.871	2.109	1.91
Al	3.983	4.035	4.011	4.018	4.038	3.438	3.817	3.431
Cu	3.522	3.633	3.565	3.595	4.545	3.474	4.027	3.524
Rh	3.759	3.831	3.781	3.794	7.563	5.688	6.642	5.783
Pd	3.844	3.942	3.876	3.876	5.016	3.714	4.435	3.938
Ag	4.002	4.145	4.050	4.062	3.642	2.516	3.078	2.985
C	3.533	3.569	3.552	3.553	9.011	7.714	8.275	7.545
SiC	4.332	4.378	4.355	4.346	**7.457**	6.401	6.876	6.478
Si	5.405	5.468	5.432	5.421	5.348	4.559	4.940	4.685
Ge	5.631	5.768	5.680	5.644	4.628	3.716	4.144	3.918
GaAs	5.615	5.752	5.665	5.640	**4.095**	3.148	3.555	3.337
LiF	3.913	4.070	4.007	3.972	**4.945**	4.322	4.474	4.457
LiCl	4.968	5.151	5.063	5.070	**3.835**	3.364	3.518	3.586
NaF	4.506	4.705	4.632	4.582	**4.384**	3.826	3.959	3.970
NaCl	5.467	5.695	5.603	5.569	**3.503**	3.097	3.223	3.337
MgO	4.170	4.261	4.223	4.189	**5.863**	4.973	5.299	5.203
ME	−0.082	0.051	−0.012		**0.642**	−0.121	0.234	
MAE	0.082	0.060	0.035		**0.642**	0.144	0.253	
MRE(%)	−1.73	1.10	−0.24		**16.50**	−3.68	5.97	
MARE(%)	1.73	1.29	0.73		**16.50**	4.23	6.52	

J. Sun *et al*, *PRB* **84**, 035117

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GGA parameterisations

$$E_{\mathrm{xc}} = \int \mathrm{d}\mathbf{r}\ \varepsilon_{\mathrm{GGA}}(n(\mathbf{r}), \nabla n(\mathbf{r}))n(\mathbf{r})$$

`XC_FUNCTIONAL : PW91`

- J. P. Perdew and Y. Wang, *PRB* **45** 13244 (1992)

`XC_FUNCTIONAL : PBE`

- J. P. Perdew, K. Burke and M Ernzerhof, *PRL* **77** 3865 (1996)

`XC_FUNCTIONAL : RPBE`

- B. Hammer, L. B. Hansen and J. K. Norskov, *PRB* **59** 7413 (1999)

`XC_FUNCTIONAL : WC`

- Z. Wu and R. E. Cohen, *PRB* **73**, 235116 (2006)

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Meta-Generalised Gradient Approximations

$$E_{\mathrm{xc}} = \int \mathrm{d}\mathbf{r}\ \varepsilon_{\mathrm{mGGA}}(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r}))n(\mathbf{r})$$

$$\tau(\mathbf{r}) = \frac{1}{2}\sum_{i=1}^{N} |\nabla\psi(\mathbf{r})|^2 \qquad V_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}}{\delta n} = V_{\mathrm{GGA}}(\mathbf{r}) + \hat{V}_{\tau}(\mathbf{r})$$

- Even more flexible functional form
- Still semi-local
- Not very successful before 2015 (SCAN: Strongly Constrained and Appropriately Normed functional)
- More theoretical limits, constraints and accurate cases explicitly built in
- Kinetic energy density: solve the Generalised Kohn-Sham equations (XC potential not multiplicative)
- Improved energetics and structural properties
- Band gaps closer to experimental ones

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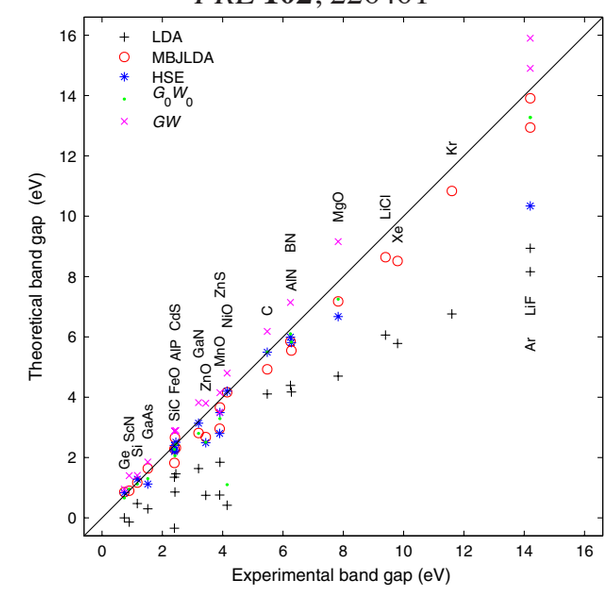
mGGA parameterisations

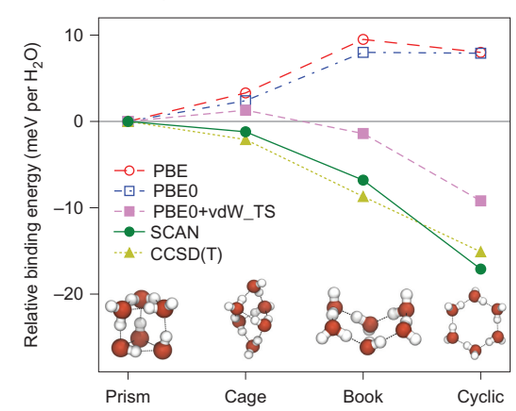
$$E_{\mathrm{xc}} = \int \mathrm{d}\mathbf{r}\ \varepsilon_{\mathrm{mGGA}}(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r}))n(\mathbf{r}) \qquad \tau(\mathbf{r}) = \frac{1}{2}\sum_{i=1}^{N} |\nabla\psi(\mathbf{r})|^2$$

$$V_{\mathrm{mBJ}}(\mathbf{r}) = V(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \tau(\mathbf{r})) \qquad V_{\mathrm{mGGA}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}}{\delta n} = V_{\mathrm{GGA}}(\mathbf{r}) + \hat{V}_{\tau}(\mathbf{r})$$

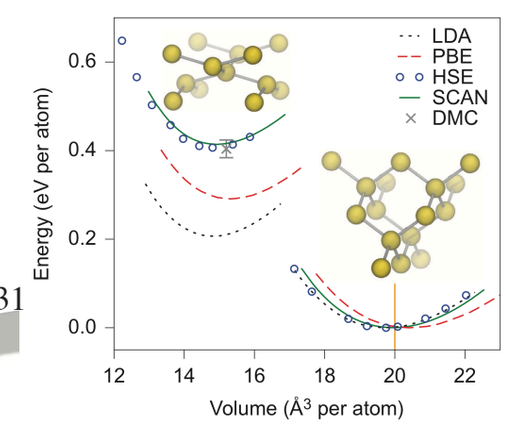
- Modified Becke-Johnson (Tran-Blaha) *potential:*
  Tran and Blaha, *PRL* **102**, 226401 (2009)
  - *potential only* mGGA, **no** total energy, **no** forces etc.
  - improves band gaps
- TPSS mGGA: Tao, Perdew, Staroverov, Scuseria,
  PRL **91**, 146401 (2003)

PRL **102**, 226401





Nat. Chem. **8**, 831



`XC_FUNCTIONAL : rSCAN`

- J. Sun, A. Ruzsinszky, J. P. Perdew
  PRL **115** 036402 (2015)
  - functional form obeys limits by construction
  - bonding situation determined based on KED
  - limiting cases are interpolated

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Hybrid functionals

$$E_{\mathrm{x,exact}} = -\frac{1}{2}\sum_{i,j}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \, \frac{\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}')\psi_j^*(\mathbf{r})\psi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$E_{\mathrm{x}} = (1-\alpha)E_{\mathrm{x,GGA}} + \alpha E_{\mathrm{x,exact}}$$

$$V_{\mathrm{x,exact}}(\mathbf{r},\mathbf{r}') = -\frac{1}{2}\sum_{j}\frac{\psi_j^*(\mathbf{r})\psi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

- Exact exchange: corresponds to the exchange energy of non-interacting one-body orbitals - does not account for all exchange energy
- Hybrid functionals use a mix of GGA exchange and exact exchange, as well as GGA correlation
- Non-local potential: a lot more expensive in plane-waves than semi-local functionals

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Hybrid functional parameterisations

In CASTEP:

- Worse scaling with system size - more expensive
- Not all functionality present

`XC_FUNCTIONAL : B3LYP`

- P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *JPC* **98** 11623 (1994)

`XC_FUNCTIONAL : PBE0`

- C. Adamo and V. Barone, *JCP* **110** 6158 (1999)

range-separated hybrids (more efficient for metals)

`XC_FUNCTIONAL : HSE03`

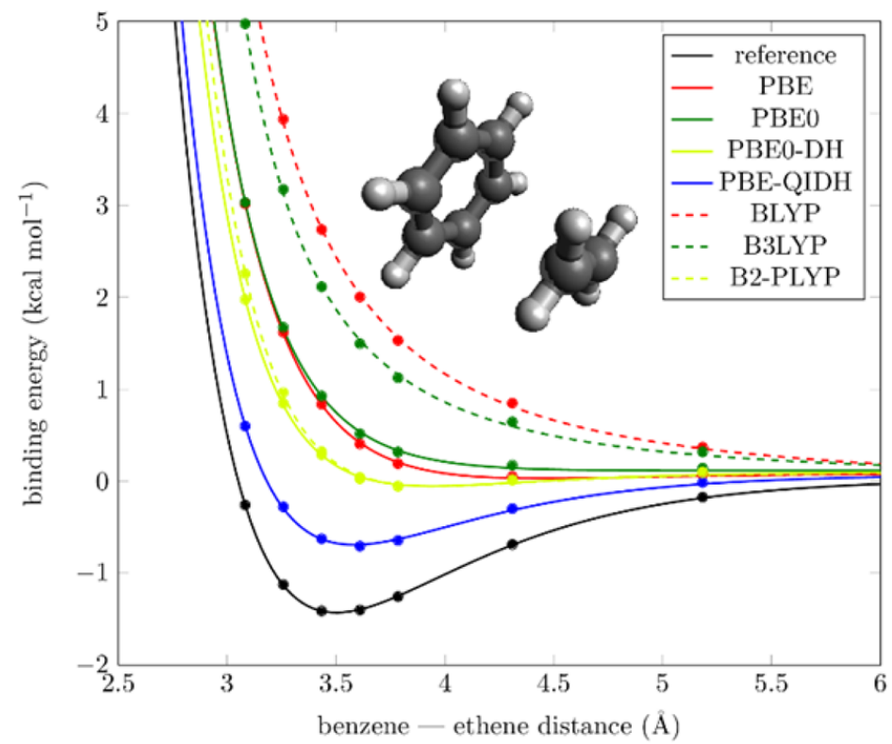
- J. Heyd, G. E. Scuseria and M. Ernzerhof, *JCP* **118** 8207 (2003)

`XC_FUNCTIONAL : HSE06`

- A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, *JCP* **125** 224106 (2006)

Double hybrid functionals

- Hybrid exchange and
- In a similar spirit to hybrids, correlation is a mix between GGA correlation and MP2 correlation
- Weak interactions (van der Waals) better described
- Not available in CASTEP



Acc. Chem. Res. **49,** 1503

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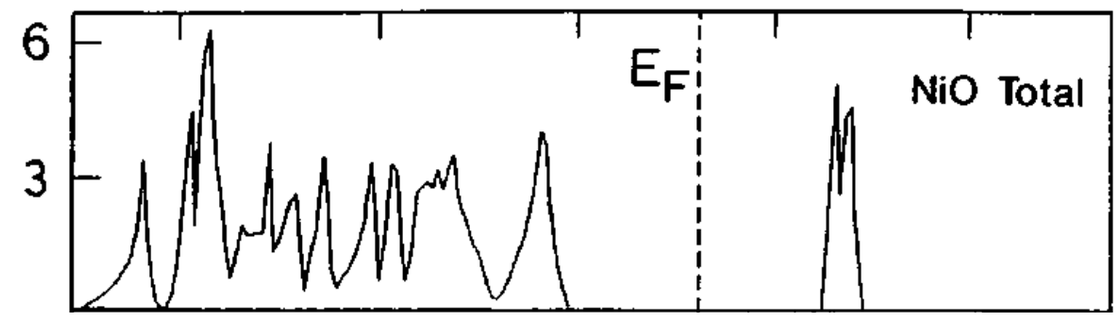
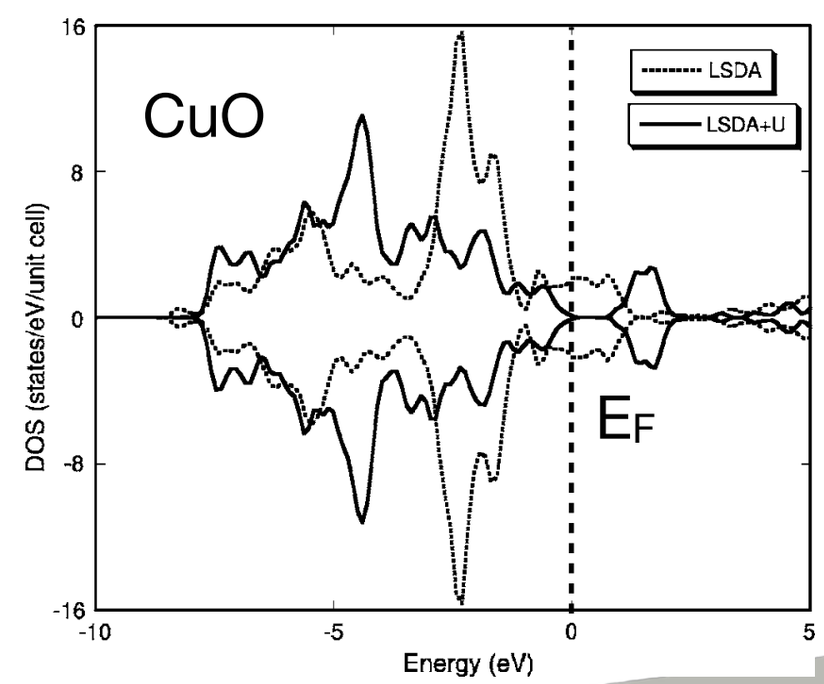
DFT+U



PRB **44,** 943

- Self-interaction error in DFT
- On-site repulsion not treated properly
- Correlation effects not modelled accurately especially in open-shell systems
- Electrons in LDA and GGA tend to be more delocalised than they should be
- meta-GGAs (SCAN) appears to improve the description of strongly correlated systems *without* U



PRB **73,** 235206

```
%block hubbard_u
Ni d:5.0
%endblock hubbard_u
```

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Dispersion corrections

- Not all correlation effects accounted for in DFT (particularly non-local correlation)
- van der Waals interactions significant in a number of systems:
  - Molecular crystals
  - Layered materials
  - Even oxides!
- Dispersion correction:
  - Pairwise schemes
  - Three-body interactions
  - TS - pairwise parameters depend on electronic structure
  - many-body dispersion

JCP **140,** 18A508

`sedc_apply : true`

`sedc_scheme : OBS`
- PRB 73, 205101 (2006)

`sedc_scheme : G06`
- (D2) J. Comput. Chem. 27, 1787 (2006)

`sedc_scheme : JCHS`
- J. Comput. Chem. 28, 555 (2007)

`sedc_scheme : TS`
- PRL 102, 073005 (2009)

`sedc_scheme : MBD*`
- J. Chem. Phys. 140, 18A508 (2014)

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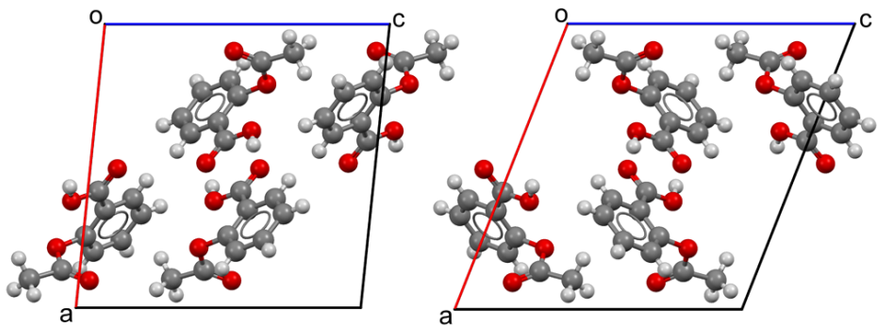
Dispersion corrections

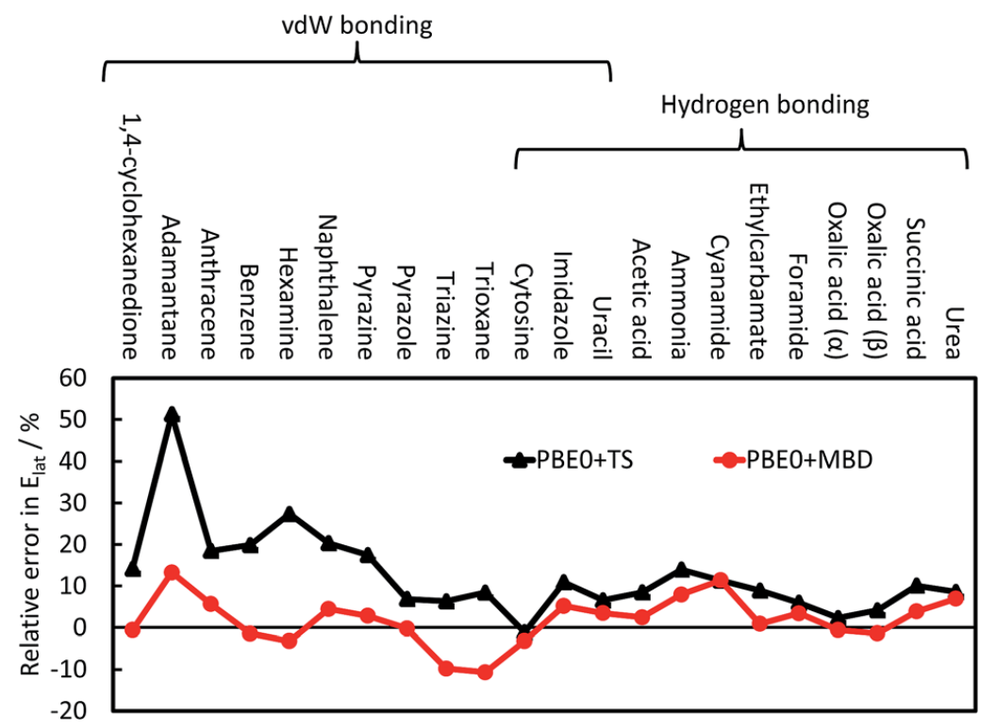
Two forms of aspirin



	$\Delta E_{\mathrm{I}\to\mathrm{II}}$/kJ/mol
PBE + TS	−0.18
PBE + TS + ZPE	−0.42
PBE + TS + F_{vib}(298 K)	−0.68
PBE + MBD	0.04
PBE + MBD + ZPE	0.35
PBE + MBD + F_{vib}(298 K)	2.56

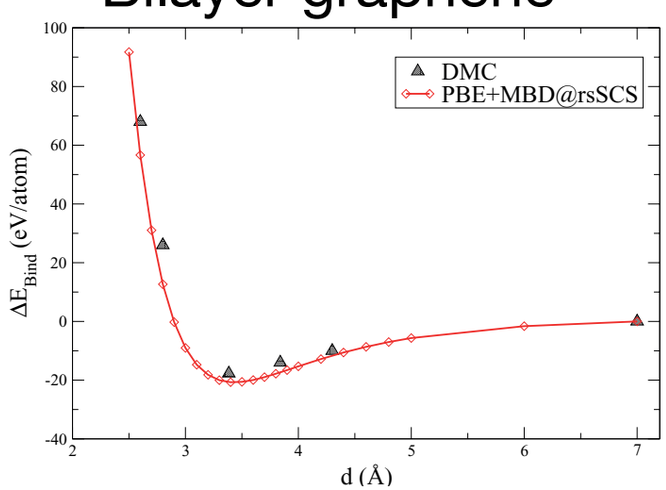
PRL **113,** 055701

Molecular crystals



Chem. Sci., **6**, 3289

Bilayer graphene



J. Phys.: Condens. Matter **28** 045201

Graphite and BN

Method	a (Å)	c (Å)	E_B (meV atom^{-1})	B_0 (GPa)	Reference
			Graphite (AB stacking)		
Expt.	2.46	6.71	43, 35 ± 10, 52 ± 5	34–42	[27, 46–48]
RPA	n.a.	6.68	48	36	[34]
PBE + MBD@ rsSCS	2.46	6.82	48	29	This work
			Graphite (AA stacking)		
RPA	n.a.	3.5	36	18	
PBE + MBD@ rsSCS	2.46	3.61	40	26	This work
			h-BN		
Expt.	2.50	6.66	—	37	[49]
RPA	n.a.	6.60	39	n.a.	[35, 50]
PBE + MBD@ rsSCS	2.50	6.59	59	30	This work

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Which functional to use?

- LDA
  - nice covalent systems
  - simple metals
- DFT+U
  - strongly correlated systems (localised *d* and *f* orbitals)
  - Mott insulators
- GGA
  - molecules
  - hydrogen-bonded materials
  - transition metals
  - magnetic systems
- Hybrid and screened hybrid exchange
  - band gaps
  - magnetic systems
- Dispersion corrected DFT (mostly GGA)
  - molecular crystals
  - layered materials
- meta-GGA
  - careful optimism: improves on most properties, including mid-range van der Waals

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