

NATIONAL CENTRE OF COMPETENCE IN RESEARCH





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Advanced functionals

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Density-functional theory

Kohn-Sham equation:

$$\left(-\frac{\hbar^2}{2m_0}\nabla^2 + V_{KS}(\mathbf{r})\right)\varphi_i(\mathbf{r}) = \varepsilon_i\,\varphi_i(\mathbf{r})$$

$$V_{KS}(\mathbf{r}) = V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) + V_{ext}(\mathbf{r})$$

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

Local density approximation (LDA):

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

Generalized-gradient approximation (GGA):

$$E_{\rm xc}^{GGA}[n] = \int \varepsilon_{\rm xc}(n(\mathbf{r}), \nabla n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}$$





Some drawbacks of LDA / GGA

Self-interaction errors

- Consequences: over-delocalization of electrons (d and f) - incorrect description of charge transfer - incorrect energetics of chemical reactions - underestimation of the band gaps

- . . .

Lack of non-locality

- Consequences: incorrect description of weak long-range (Van der Waals) interactions - inadequate description of bond breaking and formation
 - no Rydberg series

- . . .



Some advanced exchange-correlation functionals

Hubbard functionals (DFT+*U*, DFT+*U*+*V*,...)

Advanced functionals

meta-GGA (TPSS, SCAN, r2SCAN...)

Hybrid functionals (B3LYP, PBE0, HSE06,...)

van der Waals (DFT-D, DFT-D3, TS, rVV10, ...)







Self-interaction error

the approximate exchange-correlation energy terms

felt by each electron

Hartree potential $\longrightarrow V_H(\mathbf{r}) = e^2$

An electron interacts with itself \longrightarrow self-interaction (unphysical)

Self-interaction errors arrise from an incomplete cancellation of self-Coulomb terms by

$$2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$
 total charge density



Self-interaction error

The simplest example: the dissociation of H_2^+

The problem: approximate DFT gives only one solution - equal splitting of the charge



Perdew, Parr, Levy, Balduz, PRL (1982).



Self-interaction error

The simplest example: the dissociation of H_2^+

The problem: approximate DFT gives only one solution - equal splitting of the charge



Perdew, Parr, Levy, Balduz, PRL (1982).

Origin of the problem: self-interaction error (spurious quadratic energy change when adding/removing a fraction of an electron)



Cohen, Mori-Sanchez, Yang, Science (2008).









Li_{0.5}FePO₄





Li_{0.5}FePO₄

Fe²⁺: 3d⁶











Li_{0.5}FePO₄

Self-interaction error



Fe-3d electrons are delocalized and spread around



Wrong average oxidation state of 2.5+ for Fe ions





Spurious quadratic energy change when adding/removing a fraction of an electron to Fe





Li_{0.5}FePO₄

Self-interaction error



Fe-3d electrons are delocalized and spread around



Wrong average oxidation state of 2.5+ for Fe ions



Hubbard functionals



Hubbard functionals

DFT+U:
$$E = E_{\text{DFT}} + \frac{1}{2} \sum_{I,\sigma} U^{I} \operatorname{Tr} \left[(\mathbf{1} - \mathbf{n}^{I\sigma}) \mathbf{n}^{I\sigma} \right] \quad (\mathbf{n}^{I\sigma})_{m_{1}m_{2}} = \sum_{i} f_{i} \langle \psi_{i\sigma} | \varphi_{m_{2}}^{I} \rangle \langle \varphi_{m_{1}}^{I} \rangle$$

Anisimov et al., PRB (1991). Liechtenstein et al., PRB (1995).



Dudarev et al., PRB (1998).

on-site localisation (U)







Hubbard functionals

DFT+U:
$$E = E_{\text{DFT}} + \frac{1}{2} \sum_{I,\sigma} U^I \operatorname{Tr} \left[(\mathbf{1} - \mathbf{n}^{I\sigma}) \mathbf{n}^{I\sigma} \right] \quad (\mathbf{n}^{I\sigma})_{m_1m_2} = \sum_i f_i \langle \psi_{i\sigma} | \varphi_{m_2}^I \rangle \langle \varphi_{m_1}^I \rangle$$

Anisimov et al., PRB (1991).

Liechtenstein et al., PRB (1995).



$$E = E_{\text{DFT}} + \frac{1}{2} \sum_{I,\sigma} \boldsymbol{U}^{\boldsymbol{I}} \operatorname{Tr} \left[\left(\mathbf{1} - \mathbf{n}^{I\sigma} \right) \mathbf{n}^{I\sigma} \right] - \frac{1}{2} \sum_{I,J,\sigma} \boldsymbol{V}^{\boldsymbol{I}\boldsymbol{J}} \operatorname{Tr} \left[\mathbf{n}^{IJ\sigma} \mathbf{n}^{JI\sigma} \right]$$

Campo Jr and Cococcioni, JPCM (2010).



Dudarev et al., PRB (1998).





When do we need Hubbard corrections?

Alkali metals Halogens period Noble gas group Alkaline-earth metals Transition metals Rare-earth and lantha Other metals н 2 Actinoid e Other nonmetals 3 2 Li Be 11 12 3 Na Mg 6 3 5 7 8 4 19 21 22 23 24 25 26 20 4 κ Ca Sc Ti Mn V Cr Fe 42 43 44 39 40 41 37 38 5 Rb Nb Тс Sr Y Zr Мо Ru 55 57 72 74 75 76 56 73 6 Cs Ba Hf Та W Re La Os 87 88 89 107 108 104 105 106 7 Fr Rf Bh Hs Ra Db Sg Ac

Periodic table of the elements

_	58	59	60	61	62	63	64	65	66	67	68	69	70	71
ь	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
-	90	91	92	93	94	95	96	97	98	99	100	101	102	103
'	Th	Ра	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

lanthanoid series

actinoid series

C	6	2	c	
Э	C	-	•	

n elements (21, 39, 57–71)										
anoid elements (57–71 only) 2										
				13	14	15	16	17	Не	
element	S			5	6	7	8	9	10	
				В	С	Ν	0	F	Ne	
				13	14	15	16	17	18	
9	10	11	12	AI	Si	Р	S	CI	Ar	
27	28	29	30	31	32	33	34	35	36	
Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
45	46	47	48	49	50	51	52	53	54	
Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I	Хе	
77	78	79	80	81	82	83	84	85	86	
lr	Pt	Au	Hg	ТΙ	Pb	Bi	Ро	At	Rn	
109	110	111	112	113	114	115	116	117	118	
Mt	Ds	Rg	Cn	Nh	FI	Мс	Lv	Ts	Og	

When do we need Hubbard corrections?



Periodic table of the elements

lanthanoid s	series 6
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	58	59	60	61	62	63	64	65	66	67	68	69	70	71
)	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
,	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Th	Ра	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

actinoid series 7

Answer: For elements with partially filled *d* and/or *f* electrons

C	6	2	c		
5	C	7	ŝ	5	

n elements (21, 39, 57–71)									
anoid elements (57–71 only) 2									
				13	14	15	16	17	Не
element	:S			5	6	7	8	9	10
				В	С	Ν	0	F	Ne
				13	14	15	16	17	18
9	10	11	12	AI	Si	Р	S	CI	Ar
27	28	29	30	31	32	33	34	35	36
Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
45	46	47	48	49	50	51	52	53	54
Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I.	Хе
77	78	79	80	81	82	83	84	85	86
lr	Pt	Au	Hg	ТІ	Pb	Bi	Ро	At	Rn
109	110	111	112	113	114	115	116	117	118
Mt	Ds	Rg	Cn	Nh	FI	Мс	Lv	Ts	Og

Two (strongly-interconnected) key aspects of DFT+U(+V)



Hubbard parameters

Hubbard projectors





The values of Hubbard parameters are not known a priori



The values of Hubbard parameters are not known a priori

Two strategies







The values of Hubbard parameters are not known a priori

Two strategies



(Semi-)empirical

Tune *U* to reproduce, for example:

- Band gaps
- Magnetic moments
- Lattice parameters
- Oxidation enthalpies
- . . .

Requires the availability of the experimental data!





Two strategies



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Tune *U* to reproduce, for example:

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- . . .

Requires the availability of the experimental data!

- The values of Hubbard parameters are not known a priori



First-principles

- Constrained density-functional theory (cDFT)
- Constrained random phase approximation (cRPA)
- Hartree-Fock-based approaches (e.g. ACBN0)

Linear-response theory

this talk



Hubbard parameters are not universal

Computed Hubbard parameters depend on:

• Type of Hubbard projector functions (e.g. atomic, orthogonalized atomic, maximally localized Wannier functions, etc.)

 $(\mathbf{n}^{I\sigma})_{m_1m_2}$

- Oxidation state of a pseudized atom (pseudopotentials) [1]
- Exchange-correlation functional (e.g. LDA, GGA, etc.)
- Self-consistency (i.e. either "one-shot" or self-consistent)

[1] Kulik and Marzari, JCP (2008).

$$=\sum_{i}f_{i}\langle\psi_{i\sigma}|\varphi_{m_{2}}^{I}\rangle\langle\varphi_{m_{1}}^{I}|\psi_{i\sigma}\rangle$$



Hubbard parameters from linear-response theory

$$E = E_{\rm DFT} + \frac{1}{2} \, \mathbf{U} \, {\rm Tr} \left[(\mathbf{1} - \mathbf{n}) \, \mathbf{n} \right] \qquad n = {\rm Tr}[\mathbf{n}]$$

The main idea: Hubbard corrections remove spurious curvature of the total energy



Note: There is no theorem for the piece-wise linearity of E in the Hubbard manifold (only for total number of electrons)



Hubbard parameters from linear-response theory

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The main idea: Hubbard corrections remove spurious curvature of the total energy



Note: There is no theorem for the piece-wise linearity of E in the Hubbard manifold (only for total number of electrons)

$$n = Tr[n]$$



Hubbard parameters can be obtained from the following condition:



Cococcioni and de Gironcoli, PRB (2005).



Linear-response theory using supercells



Cococcioni and de Gironcoli, PRB (2005).



- Possible convergence issues when using large supercells
- Quite cumbersome to use



Modified Kohn-Sham equations:

$$\left(\hat{H}_{\sigma} + \lambda^{J} \hat{V}_{\text{pert}}^{J}\right) |\psi_{v\mathbf{k}\sigma}\rangle = \varepsilon_{v\mathbf{k}\sigma} |\psi_{v\mathbf{k}\sigma}\rangle$$

Perturbing potential:

$$\hat{V}_{\text{pert}}^{J} = \sum_{m} |\varphi_{m}^{J}\rangle\langle\varphi_{m}^{J}|$$

Cococcioni and de Gironcoli, PRB (2005).







Modified Kohn-Sham equations:

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Perturbation theory to 1st order: $(\hat{H}^{\circ}_{\sigma} - \varepsilon^{\circ}_{v\mathbf{k}\sigma}) \left| \frac{d\psi_{v\mathbf{k}\sigma}}{d\lambda^{J}} \right\rangle$ $= -\left(\frac{d\hat{V}_{\mathrm{Hxc},\sigma}}{d\lambda^{J}} - \frac{d\varepsilon_{v\mathbf{k}\sigma}}{d\lambda^{J}} + \hat{V}_{\mathrm{pert}}^{J}\right)|\psi_{v\mathbf{k}\sigma}^{\circ}\rangle$

$$V(\mathbf{r}) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \,\bar{V}_{\mathbf{q}}(\mathbf{r})$$







Modified Kohn-Sham equations:

$$\left(\hat{H}_{\sigma} + \lambda^{J}\hat{V}_{\text{pert}}^{J}\right)|\psi_{v\mathbf{k}\sigma}\rangle = \varepsilon_{v\mathbf{k}\sigma}|\psi_{v\mathbf{k}\sigma}\rangle$$

Perturbing potential:

$$\hat{V}_{\text{pert}}^{J} = \sum_{m} |\varphi_{m}^{J}\rangle\langle\varphi_{m}^{J}|$$

Response matrices

(numerical derivative using finite differences)

$$\chi_{IJ} = \frac{\Delta n^{I}}{\Delta \lambda^{J}}$$

Hubbard parameters:

 $\chi_0^{-1} - \chi^{-1})_{II} \quad V^{IJ} = (\chi_0^{-1} - \chi^{-1})_{IJ}$

Cococcioni and de Gironcoli, PRB (2005).

Perturbation theory to 1st order:

$$(\hat{H}_{\sigma}^{\circ} - \varepsilon_{v\mathbf{k}\sigma}^{\circ}) \Big| \frac{d\psi_{v\mathbf{k}\sigma}}{d\lambda^{J}} \Big\rangle$$
$$= -\left(\frac{d\hat{V}_{\mathrm{Hxc},\sigma}}{d\lambda^{J}} - \frac{d\varepsilon_{v\mathbf{k}\sigma}}{d\lambda^{J}} + \hat{V}_{\mathrm{pert}}^{J}\right) |\psi_{v\mathbf{k}\sigma}^{\circ}\rangle$$

Potential in a supercell can be decomposed into a sum over **q** points for a primitive cell:

$$V(\mathbf{r}) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \, \bar{V}_{\mathbf{q}}(\mathbf{r})$$

Response occupation matrices (from the iterative solution of the eq. above)

$$\frac{dn_{m_1m_2}^{sl\sigma}}{d\lambda^{s'l'}} = \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}}^{N_{\mathbf{q}}} e^{i\mathbf{q}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})} \Delta_{\mathbf{q}}^{s'} \bar{n}_{m_1m_2}^{s\sigma}$$



Density-functional perturbation theory (DFPT)



- Computationally much less expensive
- Easier convergence
- User-friendly and autonomous

Inspired by DFPT for phonons:

Baroni, de Gironcoli, Dal Corso, and Giannozzi, RMP (2001).

Perturbation theory to 1st order:

$$(\hat{H}_{\sigma}^{\circ} - \varepsilon_{v\mathbf{k}\sigma}^{\circ}) \left| \frac{d\psi_{v\mathbf{k}\sigma}}{d\lambda^{J}} \right\rangle$$
$$= -\left(\frac{d\hat{V}_{\mathrm{Hxc},\sigma}}{d\lambda^{J}} - \frac{d\varepsilon_{v\mathbf{k}\sigma}}{d\lambda^{J}} + \hat{V}_{\mathrm{pert}}^{J}\right) |\psi_{v\mathbf{k}\sigma}^{\circ}\rangle$$

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Comparison of the "conventional" linear response and DFPT

Scaling



Reduction of $N_{\mathbf{a}}$ in DFPT Symmetry (no equivalence in the supercell approach)

Timrov, Marzari, and Cococcioni, PRB (2018), PRB (2021), CPC (2022).

Benchmark of the equivalence between the two approaches

Method	k -mesh	SC-size/q-mesh	U(Ni-a
LR-SC	$6 \times 6 \times 6$	$2 \times 2 \times 2$	7.895
DFPT	$12 \times 12 \times 12$		7.900
LR-SC	$4 \times 4 \times 4$	$3 \times 3 \times 3$	8.146
DFPT	$12 \times 12 \times 12$		8.149
LR-SC	$3 \times 3 \times 3$	$4 \times 4 \times 4$	8.168
DFPT	$12 \times 12 \times 12$		8.172

HP code is public and is part of



) Q U A N T U M E S P R E S S O





The zoo of Hubbard projectors

1. Nonorthogonalized atomic orbitals

 $\phi_{m_1}^{I}(\mathbf{r} - \mathbf{R}_{I})$ (contained in pseudopotentials)

2. Orthogonalized atomic orbitals

$$\tilde{\phi}_{m_1}^I(\mathbf{r} - \mathbf{R}_I) = \sum_{Jm_2} \left(\hat{O}^{-\frac{1}{2}} \right)_{m_2m_1}^{JI} \phi_{m_2}^J (\mathbf{r})$$
$$\left(\hat{O} \right)_{m_1m_2}^{IJ} = \langle \phi_{m_1}^I | \phi_{m_2}^J \rangle$$

3. Maximally localized Wannier functions

$$w_{m_1}^{I}(\mathbf{r} - \mathbf{R}_{I}) = \frac{1}{\sqrt{N_{\mathbf{k}}}} \sum_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{R}_{I}} \sum_{n}^{N_{\mathrm{KSban}}}$$



Drawback:

Application of Hubbard U twice in the overlap regions

 $(\mathbf{r} - \mathbf{R}_J)$



ds

 $U_{nm_1}^{(\mathbf{k})} \psi_{n\mathbf{k}}(\mathbf{r})$







Self-consistent workflow of DFT+*U*+*V*



Timrov, Marzari, and Cococcioni, PRB (2021).





Discharging process



Li-ion batteries









Unambiguous oxidation states





Li intercalation voltages



Cococcioni and Marzari, PRM (2019).

 $\Phi = -\frac{E(\text{Li}_{x_2}S) - E(\text{Li}_{x_1}S) - (x_2 - x_1)E(\text{Li})}{(x_2 - x_1)e}$

Timrov, Aquilante, Cococcioni, Marzari, PRX Energy (2022).



Li intercalation voltages



Cococcioni and Marzari, PRM (2019).

Timrov, Aquilante, Cococcioni, Marzari, PRX Energy (2022).


Self-consistent U and V from linear-response theory



M1 - M4 = Mn1 - Mn4

HP	Mn1	Mn2	Mn3	Mn4
U	6.26	6.26	6.26	6.26
V	0.54 - 1.07	0.54 - 1.07	0.54 - 1.07	0.54-1.0





Self-consistent U and V from linear-response theory



M1 - M4 = Mn1 - Mn4

HP	Mn1	Mn2	Mn3	Mn4
U	6.26	6.26	6.26	6.26
V	0.54 - 1.07	0.54 - 1.07	0.54 - 1.07	0.54-1.0
U	6.26	6.25	6.67	5.44
V	0.40 - 1.01	0.46 - 1.05	0.54 - 1.11	0.39-1.0





Self-consistent U and V from linear-response theory



M1 - M4 = Mn1 - Mn4

_					
	HP	Mn1	Mn2	Mn3	Mn4
	U	6.26	6.26	6.26	6.26
	V	0.54 - 1.07	0.54 - 1.07	0.54 - 1.07	0.54 - 1.0
	U	6.26	6.25	6.67	5.44
	V	0.40 - 1.01	0.46 - 1.05	0.54 - 1.11	0.39 - 1.0
	U	6.42	4.95	6.41	4.94
	V	0.34 - 1.01	0.38 - 0.96	0.34 - 1.01	0.38-0.9
	U	4.67	4.64	6.58	4.98
	V	0.48 - 0.72	0.31 - 0.91	0.33 - 1.02	0.41 - 0.7
	U	4.56	4.56	4.56	4.56
	V	0.42 - 0.78	0.42 - 0.78	0.42 - 0.78	0.42-0.7

Hubbard parameters are site-dependent and change upon the (de)lithiation

How one would describe the change in U&V empirically?





Spinel cathode materials



These systems are much more expensive computationally for hybrid functionals (and less accurate), but modest for DFT+*U*+*V*





Li intercalation voltages

 $\Phi = -\frac{E(\mathrm{Li}_{x_2}\mathrm{S}) - E(\mathrm{Ii}_{x_2}\mathrm{S})}{E(\mathrm{Ii}_{x_2}\mathrm{S})} - E(\mathrm{Ii}_{x_2}\mathrm{S}) -$





$$\frac{(\text{Li}_{x_1}\text{S}) - (x_2 - x_1)E(\text{Li})}{(x_2 - x_1)e}$$

Timrov, Kotiuga, and Marzari, PCCP (2023).



Formation energies of O vacancies in perovskites



C. Ricca, I. Timrov et al., PRB (2019) & PRR (2020).



Number of atoms in the supercell

DFT+*U*+*V* accurately predicts the correct formation energies of O vacancies in the dilute limit



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Can Hubbard corrections improve band gaps?

Can we use DFT+*U*(+*V*) **to predict band gaps?**



Can Hubbard corrections improve band gaps?



By applying the Hubbard U correction to the band edges we might expect improvements in the band gap values with respect to standard DFT

High-throughput search of novel materials for H₂ production

18 out of 70150 materials were identified as candidates for the photocatalytic water splitting

Xiong, ..., Timrov,..., Dabo, Energy Environ. Sci. (2021).

	Space group	$\begin{array}{l} \textbf{DFT} \ \varepsilon_{g} \\ \textbf{(eV)} \end{array}$	DFT+ $U \varepsilon_{\rm g}$ (eV)	Exp (eV
Oxides				
$SrCu_2O_2$	I4 ₁ /amd	1.81	3.11	3.3
$BaCu_2O_2$	I4 ₁ /amd	1.39	3.22	
CuAlO ₂	$R\bar{3}m$	1.78	3.07	2.9
$CuGaO_2$	$R\bar{3}m$	0.75	2.46	1.9
$Ca_{12}Al_{14}O_{33}$	C2	2.01	3.73	4.1
Na_3BiO_4	P2/c	1.04	2.21	2.6
Sr_2PbO_4	Pbam	1.43	2.31	1.7
Sulfides				
Cu ₃ SbS ₃	$P2_{1}2_{1}2_{1}$	1.06	1.89	
Cu_2WS_4	$P\bar{4}2m$	1.66	2.06	1.7
Cu_3NbS_4	$P\bar{4}3m$	1.81	1.97	2.5
CuYS ₂	Pnma	1.63	2.18	
Oxychalcogenide	S			
LaOCuS	P4/nmm	1.70	2.65	3.1
LaOCuSe	P4/nmm	1.48	2.44	2.8
$La_4O_4Se_3$	Amm2	2.01	2.04	1.9
Na ₂ TeO ₄	$P2_{1}/c$	1.39	3.30	
Oxynitrides				
CaTaO ₂ N	$Pmc2_1$	1.67	2.46	2.6
LaTiO ₂ N	$I2_{1}2_{1}2_{1}$	1.36	2.42	2.1
Others				
$Na_5CuO_2(OH)_2$	Pnma	1.49	3.64	
$Na_5CuO_2(OH)_2$	Pnma	1.49	3.64	

Accurate vibrational energies of complex oxides

Hubbard corrections are crucial for the correct insulating ground state and dynamical stability of CoO

A. Floris, I. Timrov et al., PRB (2020).

- U and V from DFPT \longrightarrow train the machine learning model [1]
- DFPT calculation of U takes less time than HSE06 [2]

Formula	No. of Atoms	k-Points	U Calcu	lation	HSE0	6 Calcul	ation	Ratio
ronnuia	per Unit Cell	Mesh	q-Points	t_U	q-Points	$E_{ m g}$	$t_{ m HSE06}$	$t_{ m HSE06}/t_U$
TiO ₂	6	$9 \times 6 \times 6$	$4 \times 3 \times 3$	3h 46m	$3 \times 2 \times 2$	3.30	10h 1m	2.7
NbNO	12	$6 \times 6 \times 6$	$3 \times 2 \times 2$	7h 35m	$2 \times 2 \times 2$	2.68	61h 52m	8.2

[1] Uhrin, Zadoks, Binci, Marzari, Timrov, in preparation.

• When U (and V) are provided, DFT+U(+V) is only marginally more expensive than DFT

Calculation of U and V from DFPT is ~20x more expensive than the ground-state DFT

[2] Kirchner-Hall, Zhao, Xiong, Timrov, Dabo, Appl. Sci. (2021).

Limitations/open questions of linear-response theory (LRT) for U and V

- Hubbard functionals are not variational w.r.t. U and V (no theorem/proof)

• DFT+U(+V) is a mean-field single-determinant approach (no strong correlations)

Piece-wise linearity in the Hubbard manifold is heuristic (no proof)

• For closed shells (i.e. fully occupied manifolds) the U values from LRT are too large

• U and V are position-dependent \longrightarrow dU/dR \neq 0, dV/dR \neq 0 \longrightarrow extra terms in forces

Hybrid functionals

correlation functionals

 $E_{\rm Fock}$ is computationally very expensive in the plane-wave basis set

Main idea

Mixing the Fock energy (of the Hartree-Fock method) with the (semi-)local exchange-

$$\frac{\psi_{v,\mathbf{k}}^{*}(\mathbf{r})\psi_{v',\mathbf{k}'}(\mathbf{r})\psi_{v',\mathbf{k}'}(\mathbf{r}')\psi_{v,\mathbf{k}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d$$

PBE0 hybrid functional

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

correlation GGA-PBE energy

 $\alpha = 0.25$

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

100% of the (semi-local) correlation GGA-PBE energy

Electronic atomization energies (i.e. energy required to completely separate a molecule into its constituent atoms) in kcal/mol

Molecule	PBE	PBE0	Expt.
N ₂	244	225	227
02	143	124	118
SO	142	128	122

PBE0 hybrid functional gives much more accurate results than PBE compared to experiments on simple molecules

J. Paier, R. Hirschl, M. Marsman, G. Kresse, JCP 122, 234102 (2005).

Molecules

	Ρ	BE	PI	BE0	Exj	pt. [‡]
Solid	a_0	B_0	a_0	<i>B</i> ₀	a_0	B_0
Li	3.438	13.7	3.463	13.7	3.477	13.0
Na	4.200	7.80	4.229	8.22	4.225	7.5
Al	4.040	76.6	4.012	86.0	4.032	79.4
BN	3.626	370	3.600	402	3.616	400
BP	4.547	160	4.520	174	4.538	165
С	3.574	431	3.549	467	3.567	443
Si	5.469	87.8	5.433	99.0	5.430	99.2
SiC	4.380	210	4.347	231	4.358	225
β-GaN	4.546	169	4.481	199	4.520	210
GaP	5.506	75.3	5.446	87.3	5.451	88.7
GaAs	5.752	59.9	5.682	72.7	5.648	75.6
LiF	4.068	67.3	4.011	72.8	4.010	69.8

PBE0 provides more accurate results than PBE for the lattice parameters and bulk modulus of solids

J. Paier, M. Marsman, K. Hummer, G. Kresse, I.C. Gerber, J.G. Angyan, JCP 124, 154709 (2006).

Solids

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		PBE	PBE0	Expt.
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			GaAs	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Gamma_{15\nu} \rightarrow \Gamma_{1c}$	0.56	2.01	1.52^{a}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Gamma_{15\nu} \rightarrow X_{1c}$	1.46	2.67	1.90 ^a
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Gamma_{15v} \rightarrow L_{1c}$	1.02	2.37	1.74 ^a
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			Si	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Gamma_{25v}' \rightarrow \Gamma_{15c}$	2.57	3.97	3.34–3.36, ^b 3.05 ^c
$\begin{split} \Gamma_{25v}' \to L_{1c} & 1.54 & 2.88 & 2.06(3) \\ \Gamma_{25v}' \to \Gamma_{15} & 5.59 & 7.69 & 7.3^{a} \\ \Gamma_{25v}' \to X_{1c} & 4.76 & 6.66 \\ \Gamma_{25v}' \to L_{1c} & 8.46 & 10.77 \\ & MgO \\ \Gamma_{15} \to \Gamma_{1} & 4.75 & 7.24 & 7.7^{g} \\ X_{4'} \to \Gamma_{1} & 9.15 & 11.67 \\ L \to \Gamma_{1} & 7.91 & 10.38 \\ \end{split}$	$\Gamma'_{25v} \rightarrow X_{1c}$	0.71	1.93	1.13, ^d 1.25 ^c
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Gamma'_{25\nu} \rightarrow L_{1c}$	1.54	2.88	2.06(3), ^e
$\begin{array}{cccccc} & & & & & & \\ \Gamma_{25\nu}' \rightarrow \Gamma_{15} & & 5.59 & 7.69 & 7.3^{a} \\ \Gamma_{25\nu}' \rightarrow X_{1c} & & 4.76 & 6.66 \\ \Gamma_{25\nu}' \rightarrow L_{1c} & & 8.46 & 10.77 \\ & & & & \\ & & & \\ \Gamma_{15} \rightarrow \Gamma_{1} & & 4.75 & 7.24 & 7.7^{g} \\ X_{4'} \rightarrow \Gamma_{1} & & 9.15 & 11.67 \\ L_{4} \rightarrow \Gamma_{4} & & 7.91 & 10.38 \\ \end{array}$	200			$2.40(15)^{\rm f}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			С	
$ \begin{array}{ccccccccccccccccccccccccccccccccccc$	$\Gamma_{25\nu}' \rightarrow \Gamma_{15}$	5.59	7.69	7.3 ^a
$ \begin{array}{cccc} \Gamma_{25\nu}' \to L_{1c} & 8.46 & 10.77 \\ & & MgO \\ \Gamma_{15} \to \Gamma_{1} & 4.75 & 7.24 & 7.7^{g} \\ X_{4\prime} \to \Gamma_{1} & 9.15 & 11.67 \\ L_{4} \to \Gamma_{4} & 7.91 & 10.38 \end{array} $	$\Gamma'_{25\nu} \rightarrow X_{1c}$	4.76	6.66	
MgO $\Gamma_{15} \rightarrow \Gamma_{1}$ 4.75 7.24 7.7^{g} $X_{4'} \rightarrow \Gamma_{1}$ 9.15 11.67 $I \rightarrow \Gamma_{4}$ 7.91 10.38	$\Gamma'_{25v} \rightarrow L_{1c}$	8.46	10.77	
$ \begin{array}{ccc} \Gamma_{15} \rightarrow \Gamma_{1} & 4.75 & 7.24 & 7.7^{g} \\ X_{4'} \rightarrow \Gamma_{1} & 9.15 & 11.67 \\ L_{*} \rightarrow \Gamma_{*} & 7.91 & 10.38 \end{array} $			MgO	
$X_{4'} \rightarrow \Gamma_1$ 9.15 11.67 $L_{+} \rightarrow \Gamma_{-}$ 7.91 10.38	$\Gamma_{15} \rightarrow \Gamma_1$	4.75	7.24	7.7 ^g
$L \rightarrow \Gamma$ 7.91 10.38	$X_{4'} \rightarrow \Gamma_1$	9.15	11.67	
L_1 / L_1 10.50	$L_1 \rightarrow \Gamma_1$	7.91	10.38	

gaps

Direct and indirect band

J. Paier, M. Marsman, K. Hummer, G. Kresse, I.C. Gerber, J.G. Angyan, JCP 124, 154709 (2006).

• PBE underestimates band gaps

 PBE0 predicts more accurate band gaps, but this is not systematic and there are overestimations

 Overestimation of band gaps in PBE0 is related to the non-optimal fraction of the Fock exchange (see next slides)

B3LYP hybrid functional

$$\alpha = 0.20, \beta = 0.72, \gamma = 0.81$$


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A.D. Becke, JCP 98, 1372 (1993).
P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, JPC 98, 11623 (1994).
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$$P^{A} + \beta \Delta E_{x}^{B88} + \gamma E_{c}^{LYP} + (1 - \gamma) E_{c}^{LD}$$

81% of the (local) correlation GGA-LYP energy

Becke's gradient correction to the exchange functional

19% of the (local) correlation LDA energy

Molecules

	MP2			T/B3L	YP		$expt^b$		
ν	D	R	ν	D	R	ν	D		
1528	14	-5	1500	13	-5	1453	25		
1516	8	4	1489	8	5	1441	3		
1479	47	-11	1462	43	-11	1419	35		
1438	52	11	1422	51	11	1387	58		
1394	52	27	1389	50	28	1350	40		
1320	97	9	1316	112	3	1284	161		
1230	47	-11	1229	44	-4	1198	47	_	
1216	14	0	1204	19	-5	1178	35	_	
1146	191	82	1137	327	99	1118	483		
1125	219	-40	1113	87	-58	1099	51	_	
1077	10	-12	1076	11	-6	1055	40	_	
1056	271	-50	1041	268	-50	1022	251	—	
973	126	10	966	91	7	959	70		
914	9	-29	914	8	-27	896	10	_	
873	221	33	850	310	46	836	371		
829	97	26	817	34	10	812	55		
714	3	-3	712	2	2	711	13		

^{*a*} Frequencies, ν , in cm⁻¹, dipole strengths D in 10⁻⁴⁰ esu² cm², and rotational strengths R in 10^{-44} esu² cm². R values are for (R)-(+)-1.

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

Frequencies (ν), dipole strengths (D), rotational strengths (R) of 4-methyl-2-oxetanone

The Coulomb potential is partitioned as a sum of the short-range (SR) and long-range (LR) parts:

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{\operatorname{erfc}(\omega|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} + \frac{\operatorname{erf}(\omega|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}$$

Range-separated hybrid functional

Range separation

From PBE0 to HSE hybrid functional

$$E_{\rm xc}^{\rm PBE0} = \alpha E_{\rm x}^{\rm Fock} + (1 - \alpha) E_{\rm x}^{\rm PBE} + E_{\rm c}^{\rm PBE}$$

$$E_{\mathrm{xc}}^{\mathrm{HSE06}} = \alpha E_{\mathrm{x}}^{\mathrm{Fock,SR}} + (1-\alpha) E_{\mathrm{x}}^{\mathrm{PBE,SR}} + \frac{E_{\mathrm{x}}^{\mathrm{PBE,LR}} + E_{\mathrm{c}}^{\mathrm{PBE}}}{\varepsilon}$$

J. Heyd, G.E. Scuseria, M. Ernzerhof, JCP 118, 8207 (2003); JCP 124, 219906 (2006).

	PBE	PBE0	HSE03	Expt.
		GaAs		
$\Gamma_{15\nu} \rightarrow \Gamma_{1c}$	0.56	2.01	1.29	1.52^{a}
$\Gamma_{15v} \rightarrow X_{1c}$	1.46	2.67	1.99	1.90 ^a
$\Gamma_{15v} \rightarrow L_{1c}$	1.02	2.37	1.64	1.74 ^a
		Si		
$\Gamma_{25v}' \rightarrow \Gamma_{15c}$	2.57	3.97	3.19	3.34–3.36, ^b
200				3.05 ^c
$\Gamma'_{25v} \rightarrow X_{1c}$	0.71	1.93	1.23	$1.13,^{d}1.25^{c}$
$\Gamma'_{25v} \rightarrow L_{1c}$	1.54	2.88	2.13	$2.06(3),^{e}$
				$2.40(15)^{\rm f}$
		С		
$\Gamma_{25v}' \rightarrow \Gamma_{15}$	5.59	7.69	6.77	7.3 ^a
$\Gamma'_{25v} \rightarrow X_{1c}$	4.76	6.66	5.76	
$\Gamma'_{25v} \rightarrow L_{1c}$	8.46	10.77	9.80	
		MgO		
$\Gamma_{15} \rightarrow \Gamma_1$	4.75	7.24	6.34	7.7 ^g
$X_{4'} \rightarrow \Gamma_1$	9.15	11.67	10.79	
$L_1 \rightarrow \Gamma_1$	7.91	10.38	9.49	

J. Paier, M. Marsman, K. Hummer, G. Kresse, I.C. Gerber, J.G. Angyan, JCP 124, 154709 (2006).

Direct and indirect band gaps

Solids

What fraction of Fock exchange to use in solids (α parameter)?

From the analogy with the many-body perturbation theory, one can realize that:

J.H. Skone, M. Govoni, G. Galli, PRB 89, 195112 (2014).

 ϵ_{∞} is the electronic dielectric constant of a material

Dielectric constant ϵ_{∞} of solids

Material	ϵ_{∞}
Ge	15.9
Si	11.9
AlP	7.54
SiC	6.52
TiO ₂	6.34
NiO	5.76
С	5.70
CoO	5.35
GaN	5.30
ZnS	5.13
MnO	4.95
WO_3	4.81

J.H. Skone, M. Govoni, G. Galli, PRB 89, 195112 (2014).

Material	ϵ_{∞}
BN	4.50
HfO ₂	4.41
AlN	4.18
ZnO	3.74
Al_2O_3	3.10
MgO	2.96
LiCl	2.70
NaC1	2.40
LiF	1.90
H_2O	1.72
Ar	1.66
Ne	1.23

Band gaps of solids

Material	PBE	PBE0 ($\alpha = 0.25$)	PBE0 modified ($\alpha = 1/\epsilon_{\infty}$)	Expt.
Ge	0.00	1.53	0.77	0.74
Si	0.62	1.75	1.03	1.17
AlP	1.64	2.98	2.41	2.51
SiC	1.37	2.91	2.33	2.39
TiO ₂	1.81	3.92	3.18	3.3
NiO	0.97	5.28	4.61	4.3
С	4.15	5.95	5.44	5.48
CoO	0.00	4.53	4.01	2.5
GaN	1.88	3.68	3.30	3.29
ZnS	2.36	4.18	3.85	3.91
MnO	1.12	3.87	3.66	3.9
WO ₃	1.92	3.79	3.50	3.38

J.H. Skone, M. Govoni, G. Galli, PRB 89, 195112 (2014).

J.H. Skone, M. Govoni, G. Galli, PRB 93, 235106 (2016).

Calculation of the Fock energy in practice

This allows us to speed up significantly the calculation of $E_{
m x}^{
m Fock}$

$$rac{\psi_{v,\mathbf{k}}^{*}(\mathbf{r})\psi_{v',\mathbf{k}'}(\mathbf{r})\psi_{v',\mathbf{k}'}^{*}(\mathbf{r}')\psi_{v,\mathbf{k}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}$$

auxiliary q point grid ($\mathbf{q} = \mathbf{k} - \mathbf{k}'$)

Replace one sum over k points with a sum over q points ($N_{\mathbf{q}} \leq N_{\mathbf{k}}$)

 $E_{\mathbf{x}}^{\text{Fock}} = -\frac{1}{2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{v} \sum_{v} \int_{v'} \int \int \frac{\psi_{v,\mathbf{k}'}^*(\mathbf{r})\psi_{v',\mathbf{k}'}(\mathbf{r})\psi_{v,\mathbf{k}'}(\mathbf{r}')\psi_{v,\mathbf{k}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$

$$E_{\mathbf{x}}^{\mathbf{Fock}} = -\frac{1}{2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{v} \sum_{v'} \int_{v'} \int$$

 $\frac{\psi_{v,\mathbf{k}}^{*}(\mathbf{r})\psi_{v',\mathbf{k}'}(\mathbf{r})\psi_{v',\mathbf{k}'}(\mathbf{r}')\psi_{v,\mathbf{k}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$

$$E_{\mathbf{x}}^{\text{Fock}} = -\frac{1}{2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{v} \sum_{v'} \int \int \frac{\psi_{v,\mathbf{k}}^{*}(\mathbf{r})\psi_{v',\mathbf{k}'}(\mathbf{r})\psi_{v,\mathbf{k}'}(\mathbf{r}')\psi_{v,\mathbf{k}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$= -\frac{2\pi}{\Omega} \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}} \sum_{\mathbf{G}} \frac{A(\mathbf{q} + \mathbf{G})}{|\mathbf{q} + \mathbf{G}|^{2}}, \qquad A(\mathbf{q} + \mathbf{G}) = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \sum_{v,v'} |\rho_{v,\mathbf{k}}^{v',\mathbf{k}-\mathbf{q}}(\mathbf{q} + \mathbf{G})|$$

$$\rho_{v,\mathbf{k}}^{v',\mathbf{k}-\mathbf{q}}(\mathbf{r}) = u_{v',\mathbf{k}-\mathbf{q}}^{*}(\mathbf{r}) u_{v,\mathbf{k}}(\mathbf{r})$$

$$E_{\mathbf{x}}^{\text{Fock}} = -\frac{1}{2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{v} \sum_{v'} \int \int \frac{\psi_{v,\mathbf{k}}^{*}(\mathbf{r})\psi_{v',\mathbf{k}'}(\mathbf{r})\psi_{v',\mathbf{k}'}(\mathbf{r}')\psi_{v,\mathbf{k}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$\Rightarrow$$

$$Pock = -\frac{2\pi}{\Omega} \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}} \sum_{\mathbf{G}} \frac{A(\mathbf{q} + \mathbf{G})}{|\mathbf{q} + \mathbf{G}|^{2}}, \qquad A(\mathbf{q} + \mathbf{G}) = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \sum_{v,v'} |\rho_{v,\mathbf{k}}^{v',\mathbf{k}-\mathbf{q}}(\mathbf{q} + \mathbf{G})|$$

$$\rho_{v,\mathbf{k}}^{v',\mathbf{k}-\mathbf{q}}(\mathbf{r}) = u_{v',\mathbf{k}-\mathbf{q}}^{*}(\mathbf{r}) u_{v,\mathbf{k}}(\mathbf{r})$$

$$\psi_{v,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N_{\mathbf{k}}}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{v,\mathbf{k}}(\mathbf{r})$$

$$E_{\mathbf{x}}^{\text{Fock}} = -\frac{1}{2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{v} \sum_{v'} \int \int \frac{\psi_{v,\mathbf{k}}^{*}(\mathbf{r})\psi_{v',\mathbf{k}'}(\mathbf{r}')\psi_{v,\mathbf{k}'}(\mathbf{r}')\psi_{v,\mathbf{k}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$= -\frac{2\pi}{\Omega} \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}} \sum_{\mathbf{G}} \frac{A(\mathbf{q} + \mathbf{G})}{|\mathbf{q} + \mathbf{G}|^{2}},$$

$$A(\mathbf{q} + \mathbf{G}) = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \sum_{v,v'} |\rho_{v,\mathbf{k}}^{v',\mathbf{k}-\mathbf{q}}(\mathbf{q} + \mathbf{G})|$$

$$p_{v,\mathbf{k}}^{v',\mathbf{k}-\mathbf{q}}(\mathbf{r}) = u_{v',\mathbf{k}-\mathbf{q}}^{*}(\mathbf{r}) u_{v,\mathbf{k}}(\mathbf{r})$$

$$\psi_{v,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N_{\mathbf{k}}}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{v,\mathbf{k}}(\mathbf{r})$$

Gygi-Baldereschi method to treat the q+G=0 singulatiry

 $E_{\mathbf{x}}^{\text{Fock}} = -\frac{2\pi}{\Omega} \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}} \sum_{\mathbf{G}} \frac{A(\mathbf{q} + \mathbf{G})}{|\mathbf{q} + \mathbf{G}|^2}$

F. Gygi and A. Baldereschi, PRB 34, 4405 (1986).

H.-V. Nguyen and S. de Gironcoli, PRB 79, 205114 (2009).

Gygi-Baldereschi method to treat the q+G=0 singulatiry

$$E_{\mathbf{x}}^{\text{Fock}} = -\frac{2\pi}{\Omega} \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}} \sum_{\mathbf{G}} \frac{A(\mathbf{q} + \mathbf{G})}{|\mathbf{q} + \mathbf{G}|}$$
$$= -\frac{2\pi}{\Omega} \left\{ \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q},\mathbf{G}} \frac{A(\mathbf{q} + \mathbf{G})}{|\mathbf{G}|} \right\}$$

We are adding and subtracting exactly the same term (in red)

F. Gygi and A. Baldereschi, PRB 34, 4405 (1986).

H.-V. Nguyen and S. de Gironcoli, PRB 79, 205114 (2009).

Gygi-Baldereschi method to treat the q+G=0 singulatiry

$$E_{\mathbf{x}}^{\text{Fock}} = -\frac{2\pi}{\Omega} \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}} \sum_{\mathbf{G}} \frac{A(\mathbf{q} + \mathbf{G})}{|\mathbf{q} + \mathbf{G}|^{2}}$$

$$= -\frac{2\pi}{\Omega} \left\{ \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q},\mathbf{G}} \frac{A(\mathbf{q} + \mathbf{G}) - A(\mathbf{0})e^{-\alpha|\mathbf{q} + \mathbf{G}|^{2}}}{|\mathbf{q} + \mathbf{G}|^{2}} + \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q},\mathbf{G}} \frac{e^{-\alpha|\mathbf{q} + \mathbf{G}|^{2}}}{|\mathbf{q} + \mathbf{G}|^{2}} A(\mathbf{0}) \right\}$$

$$= -\frac{2\pi}{\Omega} \left\{ \frac{1}{N_{\mathbf{q}}} \left[\sum_{\mathbf{q},\mathbf{G}} \frac{A(\mathbf{q} + \mathbf{G}) - A(\mathbf{0})e^{-\alpha|\mathbf{q} + \mathbf{G}|^{2}}}{|\mathbf{q} + \mathbf{G}|^{2}} + \lim_{\mathbf{q} \to \mathbf{0}} \frac{A(\mathbf{q}) - A(\mathbf{0})}{|\mathbf{q}^{2}} \right] + \mathbf{D} \times A(\mathbf{0}) \right\}$$

$$D = \frac{1}{N_{\mathbf{q}}} \left[-\sum_{\mathbf{q},\mathbf{G}}^{\prime} \frac{e^{-\alpha |\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2} + \alpha \right] + \frac{\Omega}{(2\pi)^3} \sqrt{\frac{\pi}{\alpha}}$$

F. Gygi and A. Baldereschi, PRB 34, 4405 (1986).

H.-V. Nguyen and S. de Gironcoli, PRB 79, 205114 (2009).

Gygi-Baldereschi method to treat the q+G=0 singulatiry

$$\begin{split} E_{\mathbf{x}}^{\text{Fock}} &= -\frac{2\pi}{\Omega} \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}} \sum_{\mathbf{G}} \frac{A(\mathbf{q} + \mathbf{G})}{|\mathbf{q} + \mathbf{G}|^{2}} \\ &= -\frac{2\pi}{\Omega} \left\{ \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q},\mathbf{G}} \frac{A(\mathbf{q} + \mathbf{G}) - A(0)e^{-\alpha|\mathbf{q} + \mathbf{G}|^{2}}}{|\mathbf{q} + \mathbf{G}|^{2}} + \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q},\mathbf{G}} \frac{e^{-\alpha|\mathbf{q} + \mathbf{G}|^{2}}}{|\mathbf{q} + \mathbf{G}|^{2}} A(0) \right\} \\ &= -\frac{2\pi}{\Omega} \left\{ \frac{1}{N_{\mathbf{q}}} \left[\sum_{\mathbf{q},\mathbf{G}} \frac{A(\mathbf{q} + \mathbf{G})}{|\mathbf{q} + \mathbf{G}|^{2}} + \lim_{\mathbf{q} \to 0} \frac{A(\mathbf{q}) - A(0)}{\mathbf{q}^{2}} \right] + D \times A(0) \right\} \\ &= no \mathbf{q} + \mathbf{G} = 0 \text{ singularity,} \\ \text{straightforward to compute} \\ \end{split}$$
 non-analytic limit 0/0 \\ \text{can be dealt with using} \\ \end{split}

F. Gygi and A. Baldereschi, PRB 34, 4405 (1986).

different techniques (e.g. extrapolation)

ally

H.-V. Nguyen and S. de Gironcoli, PRB 79, 205114 (2009).



meta-GGA functionals



$$E_{\rm xc}[n_{\uparrow},n_{\downarrow}] = \int d^3r \, \boldsymbol{n}(\mathbf{r}) \, \varepsilon_{\rm xc} \Big(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), \nabla n_{\uparrow}(\mathbf{r}), \nabla n_{\downarrow}(\mathbf{r}), \nabla^2 n_{\uparrow}(\mathbf{r}), \nabla^2 n_{\downarrow}(\mathbf{r}), \tau_{\uparrow}(\mathbf{r}), \tau_{\downarrow}(\mathbf{r}), \tau_{\downarrow}(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{\sigma} n_{\sigma}(\mathbf{r})$$
 total characteristics

$$n_{\sigma}(\mathbf{r}) = \sum_{v,\mathbf{k}} |\psi_{v,\mathbf{k}}^{\sigma}(\mathbf{r})|^2$$
 spin-ch

$$au_{\sigma}(\mathbf{r}) = rac{1}{2} \sum_{v,\mathbf{k}} |
abla \psi^{\sigma}_{v,\mathbf{k}}(\mathbf{r})|^2 \quad ext{kinetic}$$

Main idea

harge density

harge density

 $\sigma = \{\uparrow, \downarrow\}$

energy density





Different meta-GGA functionals



























SCAN, rSCAN, r²SCAN

$$E_{\rm xc}[n_{\uparrow},n_{\downarrow}] = \int d^3r \, n(\mathbf{r}) \, \varepsilon_{\rm xc}\Big(n_{\uparrow}(\mathbf{r}),n_{\downarrow}(\mathbf{r}),$$



 $abla n_{\uparrow}(\mathbf{r}),
abla n_{\downarrow}(\mathbf{r}),
abla^2 n_{\uparrow}(\mathbf{r}),
abla^2 n_{\downarrow}(\mathbf{r}),
abla_{\downarrow}(\mathbf{r}),
abla_{\downarrow}$



SCAN: J. Sun et al., Phys. Rev. Lett. 115, 036402 (2015). rSCAN: A. Bartok et al., J. Chem. Phys. 150, 161101 (2019). r²SCAN: J. Furness et al., J. Phys. Chem. Lett. **11**, 8208 (2020).







Accuracy of the SCAN meta-GGA functional

"SCAN" stands for Strongly Constrained and Appropriately Normed functional SCAN obeys all 17 known exact constraints

	G 3 ^{HC} (kcal/mol)		G (kcal/	G3 BF cal/mol) (kcal		[76 /mol)	S22 (kcal/mol)		LC2
	ME	MAE	ME	MAE	ME	MAE	ME	MAE	ME
LSDA	-5.6	13.0	-83.7	83.7	-15.2	15.4	2.3	2.3	-0.081
BLYP	1.8	6.2	3.8	9.5	-7.9	7.9	-8.7	8.8	
PBEsol	-4.1	6.5	-58.7	58.8	-11.5	11.5	-1.3	1.8	-0.012
PBE	-2.1	6.6	-21.7	22.2	-9.1	9.2	-2.8	2.8	0.05
TPSS	1.9	3.8	-5.2	5.8	-8.6	8.7	-3.7	3.7	0.03
M06 L	-0.2	4.6	-1.6	5.2	-3.9	4.1	-0.9	0.9	0.01
SCAN	-0.8	2.7	-4.6	5.7	-7.7	7.7	-0.7	0.9	0.00

J. Sun, A. Ruzsinszky, J. P. Perdew, PRL 115, 036402 (2015).

20(Å) MAE 1 0.081 2 0.036 1 0.059 5 0.043 5 0.069 7 0.016

TABLE II. Mean error (ME) and mean absolute error (MAE) of SCAN and other semilocal functionals for the G3 set of molecules [73], the BH76 set of chemical barrier heights [74], the S22 set of weakly bonded complexes [69], and the LC20 set of solid lattice constants [75]. For the G3-1 subset of small molecules, the SCAN MAE is 3.2 kcal/mol. G3^{HC} is a subset of 46 G3 hydrocarbons, to which we have applied empirical corrections for the C atom as described in the text to show how consistently SCAN describes molecules. For all data sets, zero-point vibration effects have been removed from the reference experimental values. The LSDA results for G3 are from Ref. [25]. Becke-Lee-Yang-Parr (BLYP) [15,76], PBEsol [18], and PBE [6] are GGAs; SCAN, TPSS [7], and M06 L [20] are meta GGAs. We could not locate BLYP in VASP, but Ref. [77] suggests that its LC20 MAE may be more than twice that of PBE. (1 kcal/mol = 0.0434 eV.)





Regularized SCAN (rSCAN)



A.P. Bartok and J.R. Yates, JCP 150, 161101 (2019).



 f_x, f'_x, f''_x are the switching functions

rSCAN has better numerical behavior than SCAN, but it is less accurate than SCAN







Table 2. Mean Error (ME) and Mean Absolute Error (MAE) of TPSS,⁵⁹ SCAN,⁷ rSCAN,²² and r²SCAN for the G3 Set of 226 Molecular Atomization Energies,²⁸ the BH76 Set of 76 Chemical Barrier Heights,⁵⁴ the S22 set of 22 Interaction Energies between Closed Shell Complexes,⁵⁵ and the LC20 Set of 20 Solid Lattice Constants^{56a}

	G3		BH	BH76		22	LC20	
	ME	MAE	ME	MAE	ME	MAE	ME	MAE
TPSS	-5.2	5.8	-8.6	8.6	-3.4	3.4	0.033	0.041
SCAN	-5.0	6.1	-7.7	7.7	-0.5	0.8	0.009	0.015
rSCAN	-14.0	14.3	-7.4	7.4	-1.2	1.3	0.020	0.025
r ² SCAN	-4.5	5.5	-7.1	7.2	-0.9	1.1	0.022	0.027

^aErrors for G3, BH76, and S22 sets are in kcal/mol, whereas errors for LC20 are in Å. We did not make corrections for basis set superposition error for the S22 set which used the aug-cc-pVTZ basis set.⁶⁰ All calculations for G3 and BH76 used the 6-311++G(3df, 3pd) basis set.^{28,61} Details of the computational methods are included in Section S1 of the Supporting Information.

J.W. Furness, A.D. Kaplan, J. Ning, J.P. Perdew, and J. Sun, JPCL 11, 8208 (2020).







Success stories of SCAN

Material	Expt.	LDA	PBE	HSE	SCAN
Si InP GaAs BAs	1.17 1.42 1.52 1.60 ^b	0.60 0.50 0.30 1.21	0.71 0.72 0.53 1.26	1.11 1.52 1.41 1.71	0.97 1.06 0.8 1.51
CdSe BP GaP	1.73 2.10 2.35	0.44 1.36 1.53	0.71 1.43 1.69	1.71 1.66 1.79 2.09	1.10 1.74 1.94
β -GaN ZnS C ^d	2.48 3.17 3.72 5.50	0.96 1.70 1.87 4.14	1.23 1.69 2.12 4.17	2.27 2.97 3.32 4.94	1.62 2.03 2.63 4.58

SCAN provides more accurate band gaps than LDA and PBE, but less accurate than HSE

Z.-H. Yang, H. Peng, J. Sun, and J. P. Perdew, PRB 93, 205205 (2016).







Six polymorphs of MnO₂



D. A. Kitchaev, H. Peng, Y. Liu, J. Sun, J.P. Perdew, and G. Ceder, PRB 93, 045132 (2016).

Success stories of SCAN

Formation energies relative to the β phase



SCAN correctly predicts that the β phase is the lowest-energy phase



One of failures of SCAN

		V_0	B_0	B_0'	$m_s(V_0)$
		$(\text{\AA}^3/\text{at})$	(GPa)	(1)	$(\mu_{\rm B})$
	SCAN	11.58	157.5	5.05	2.66
bcc-Fe	PBE	11.35	197.7	4.45	2.20
	LSDA	10.36	253.3	4.39	1.95
	Expt.	11.64	175.1	4.6	1.98, ^b 2.08, ^c 2.13 ^a
	SCAN	10.38	230.5	4.79	0.73
fcc-Ni	PBE	10.90	199.8	4.76	0.63
	LSDA	10.06	253.6	4.77	0.58
	Expt.	10.81	192.5	4	0.52, ^c 0.55, ^d 0.57 ^a
	SCAN	10.45	262.5	4.15	1.73
hcp-Co	PBE	10.91	196.9	4.61	1.61
	LSDA	9.99	237.6	4.95	1.49
	Expt.	10.96	198.4	4.26	1.52,° 1.55, ^b 1.58 ^e

SCAN overestimates magnetic moments in itinerant ferromagnets

M. Ekholm, D. Gambino, H. J. M. Jönsson, F. Tasnádi, B. Alling, and I. A. Abrikosov, PRB 98, 094413 (2018).



van der Waals functionals



- vdW is a distance-dependent interaction between atoms or molecules
- vdW is weak, and it is different from ionic and covalent bonding
- vdW originate from correlations between charge fluctuations in different parts of an extended system (different fragments)
- vdW interactions are non-local
- vdW are not captured by LDA, GGA, meta-GGA (except SCAN for shortrange part of vdW), DFT+U, and hybrids.

van der Waals (vdW) force









Two types of vdW functionals



Empirical (or ab initio) corrections

$$C_6 R^{-6}$$

vdW functionals

Fully nonlocal functionals $\frac{1}{2} \iint n(\mathbf{r}) \Phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$





Two types of vdW functionals



Empirical (or ab initio) corrections

$$C_6 R^{-6}$$

vdW functionals

Fully nonlocal functionals

 $\frac{1}{2} \iint n(\mathbf{r}) \Phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$





Lennard-Jones potential







- Dispersion coefficients C_6^{ij} are determined empirically
- $f_{\rm dmp}$ is a damping function to avoid nearsingularities for small R_{ii} IJ

S. Grimme, J. Comput. Chem. 27, 1787 (2006).

DFT-D functional

$$\sum_{i+1}^{4} rac{C_6^{ij}}{R_{ij}^6} f_{\mathrm{dmp}}(R_{ij}), \quad f_{\mathrm{dmp}}(R_{ij}) = rac{1}{1+e^{-d(R_{ij}/R_{ij})}}$$

Element	<i>C</i> ₆	R_0	Element	<i>C</i> ₆	R_0
Н	0.14	1.001	K	10.80 ^c	1.485
He	0.08	1.012	Ca	10.80 ^c	1.474
Li	1.61	0.825	Sc–Zn	10.80 ^c	1.562 ^d
Be	1.61	1.408	Ga	16.99	1.650
В	3.13	1.485	Ge	17.10	1.727
С	1.75	1.452	As	16.37	1.760
Ν	1.23	1.397	Se	12.64	1.771
Ο	0.70	1.342	Br	12.47	1.749
F	0.75	1.287	Kr	12.01	1.727
Ne	0.63	1.243	Rb	24.67 ^c	1.628
Na	5.71 ^c	1.144	Sr	24.67 ^c	1.606
Mg	5.71 ^c	1.364	Y–Cd	24.67 ^c	1.639 ^d
Al	10.79	1.639	In	37.32	1.672
Si	9.23	1.716	Sn	38.71	1.804
Р	7.84	1.705	Sb	38.44	1.881
S	5.57	1.683	Te	31.74	1.892
Cl	5.07	1.639	Ι	31.50	1.892
Ar	4.61	1.595	Xe	29.99	1.881

V. Barone et al., J. Comput. Chem. 30, 934 (2008).







$E_{\text{DFT-D3}} = E_{\text{KS-DFT}} - E_{\text{vdW}}$

S. Grimme, J. Antony, S. Ehrlich, H. Krieg, JCP 132, 154104 (2010).

DFT-D3 functional

 $E_{\rm vdW} = E^{(2)} + E^{(3)}$







$$E_{\rm DFT-D3} = E_{\rm KS-DFT} - E_{\rm vdW}$$

Two-body term:

$$E^{(2)} = \sum_{AB} \sum_{n=6,8,10,\dots} s_n \frac{C_n^{AB}}{r_{AB}^n} f_{d,n}(r_{AB})$$

$$f_{d,n}(r_{AB}) = \frac{1}{1 + 6(r_{AB}/(s_{r,n}R_0^{AB}))^{-\alpha_n}}$$

S. Grimme, J. Antony, S. Ehrlich, H. Krieg, JCP 132, 154104 (2010).

DFT-D3 functional

 $E_{\rm vdW} = E^{(2)} + E^{(3)}$







$$E_{\rm DFT-D3} = E_{\rm KS-DFT} - E_{\rm vdW}$$

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S. Grimme, J. Antony, S. Ehrlich, H. Krieg, JCP 132, 154104 (2010).

DFT-D3 functional

$$E_{\rm vdW} = E^{(2)} + E^{(3)}$$

Three-body term:

$$E^{(3)} = \sum_{ABC} f_{d,(3)}(\overline{r}_{ABC}) E^{ABC}$$

$$E^{ABC} = \frac{C_9^{ABC} (3 \cos \theta_a \cos \theta_b \cos \theta_c + 1)}{(r_{AB} r_{BC} r_{CA})^3}$$





Tkatchenko-Scheffler (TS) functional

$$E_{\rm vdW} = -\frac{1}{2} \sum_{A,B} f_{\rm dam}$$

A. Tkatchenko and M. Scheffler, PRL 102, 073005 (2009).

 $(R_{AB}, R_A^0, R_B^0) C_{6AB} R_{AB}^{-6}$

Dispersion coefficients are computed from first principles using the electronic charge density



Tkatchenko-Scheffler (TS) functional

$$E_{\rm vdW} = -\frac{1}{2} \sum_{A,B} f_{\rm dar}$$

$$C_{6AB} = \frac{2C_{6AA}C_{6BB}}{\left[\frac{\alpha_B^0}{\alpha_A^0}C_{6AA} + \frac{\alpha_A^0}{\alpha_B^0}C_{6BB}\right]}$$
$$C_{6AA} = \frac{\eta_A^{\text{eff}}}{\eta_A^{\text{free}}} \left(\frac{\kappa_A^{\text{free}}}{\kappa_A^{\text{eff}}}\right)^2 \left(\frac{V_A^{\text{eff}}}{V_A^{\text{free}}}\right)^2 C_{6AA}^{\text{free}}$$

A. Tkatchenko and M. Scheffler, PRL 102, 073005 (2009).

 $mp(R_{AB}, R_A^0, R_B^0)C_{6AB}R_{AB}^{-6}$

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Tkatchenko-Scheffler (TS) functional

$$E_{\rm vdW} = -\frac{1}{2} \sum_{A,B} f_{\rm dar}$$

$$C_{6AB} = \frac{2C_{6AA}C_{6BB}}{\left[\frac{\alpha_B^0}{\alpha_A^0}C_{6AA} + \frac{\alpha_A^0}{\alpha_B^0}C_{6BB}\right]}$$
$$C_{6AA} = \frac{\eta_A^{\text{eff}}}{\eta_A^{\text{free}}} \left(\frac{\kappa_A^{\text{free}}}{\kappa_A^{\text{eff}}}\right)^2 \left(\frac{V_A^{\text{eff}}}{V_A^{\text{free}}}\right)^2 C_{6AA}^{\text{free}}$$

A. Tkatchenko and M. Scheffler, PRL 102, 073005 (2009).

 $mp(R_{AB}, R_A^0, R_B^0)C_{6AB}R_{AB}^{-6}$

Dispersion coefficients are computed from first principles using the electronic charge density

Hirshfeld partitioning of the electronic charge density:

$$\frac{\kappa_A^{\text{eff}}}{\kappa_A^{\text{free}}} \frac{\alpha_A^{\text{eff}}}{\alpha_A^{\text{free}}} = \frac{V_A^{\text{eff}}}{V_A^{\text{free}}} = \left(\frac{\int r^3 w_A(\mathbf{r}) n(\mathbf{r}) d^3 \mathbf{r}}{\int r^3 n_A^{\text{free}}(\mathbf{r}) d^3 \mathbf{r}}\right)$$
$$w_A(\mathbf{r}) = \frac{n_A^{\text{free}}(\mathbf{r})}{\sum_B n_B^{\text{free}}(\mathbf{r})},$$





Two types of vdW functionals



Empirical (or ab initio) corrections



vdW functionals

Fully nonlocal functionals $\frac{1}{2} \iint n(\mathbf{r}) \Phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$





 $E_c[n] =$ Nonlocal correlation energy:

 $E_c^{nl}[n]$ is defined to include the longest ranged or most nonlocal terms that give the vdW interaction and to approach zero in the limit of a slowly varying density. The term $E_c^0[n]$ is also nonlocal, but approaches the LDA in this limit.

$$\underline{E_{\mathbf{c}}^{\mathrm{nl}}} = \frac{1}{2} \int \int n(\mathbf{r}) \Phi\left(n(\mathbf{r}), n(\mathbf{r}'), |\nabla n(\mathbf{r})|, |\nabla n(\mathbf{r}')|, |\mathbf{r} - \mathbf{r}'|\right) n(\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}'$$
nonlocal kernel

There are different numerical methods and approximations how to compute $E_c^{nl}[n]$

$$E_{\rm c}^0[n] + E_{\rm c}^{\rm nl}[n]$$



vdW-DF

vdW-DF2

VV10

rVV10

M. Dion et al., PRL 92, 246401 (2004).

K. Lee et al., PRB 82, 081101(R) (2010).

O.A. Vydrov and T. Van Voorhis, JCP 133, 244103 (2010).

R. Sabatini, T. Gorni, S. de Gironcoli, PRB 87, 041108(R) (2013).



Binding energy curves for the Ar dimer



R. Sabatini, T. Gorni, S. De Gironcoli, PRB 87, 041108(R) (2013).

Examples



Ar





P.L. Silvestrelli and A. Ambrosetti, JCP 140, 124107 (2014).

Examples



Can we mix advanced functionals?



(meta-GGA) + (van der Waals) + (Hubbard U)

TABLE II. The calculated total energy with respect to the RS phase (ΔE in meV/f.u.), equilibrium volume (Ω_0 in Å³/f.u.), bulk modulus (B_0 in GPa), and fundamental band gap (E_g in eV) for MnO, FeO, CoO, and NiO in both RS and ZB structures, using PBE+TS+U and SCAN+rVV10+U. The experimental data are collected in Refs. [17,18].

			PBE+T	S+U			SCAN+rVV10+U			Experiment		
Compound		ΔE	Ω_0	B_0	E_g	ΔE	Ω_0	B_0	E_g	Ω_0	B_0	E_g
MnO	RS ZB	0 88	21.58 26.47	156 102	1.8 0.8	0 138	21.71 26.43	164 120	2.3 1.1	21.96	151–162	3.8–4.2
FeO	RS ZB	0 142	20.25 24.34	150 107	1.2 0.3	0 157	20.28 23.15	163 84	1.4 0.8	20.35	150–180	2.4
CoO	RS ZB	0 51	19.06 23.53	184 137	2.3 1.4	0 92	19.08 23.45	186 146	2.9 1.7	19.25	180	3.6
NiO	RS ZB	0 768	17.76 20.55	205 56	2.5 0.9	0 782	17.94 21.16	220 85	3.5 1.5	18.14	166–208	3.7–4.3

H. Peng and J. P. Perdew, PRB 96, 100101(R) (2017).

