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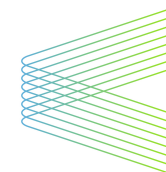
The DFT+U method for strongly-correlated and mixed-valence systems

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ONETEP Masterclass 2024

With contributions from: O. K. Orhan (Trinity), S. Berman (Trinity), A. Burgess (Trinity), N. D. E. B. Linscott (EPFL), N. Hine (Warwick), G. Teobaldi (STFC U.K.), A. A. Mostofi (Imperial), G. Moynihan (Trinity), D. Sarpa (Southampton).



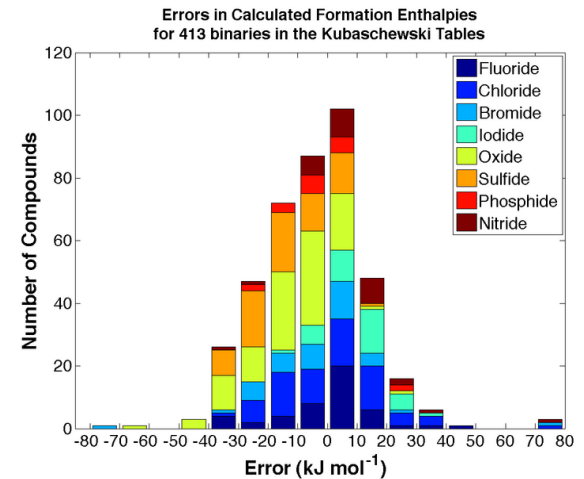
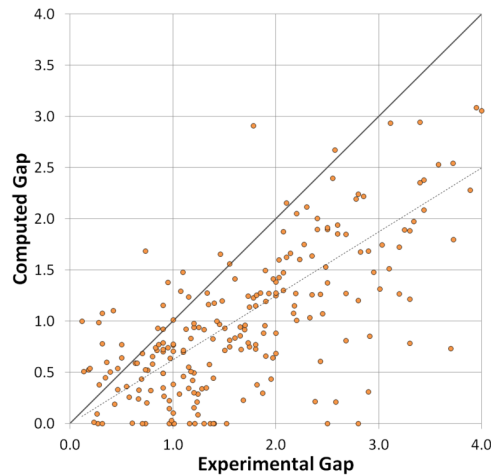
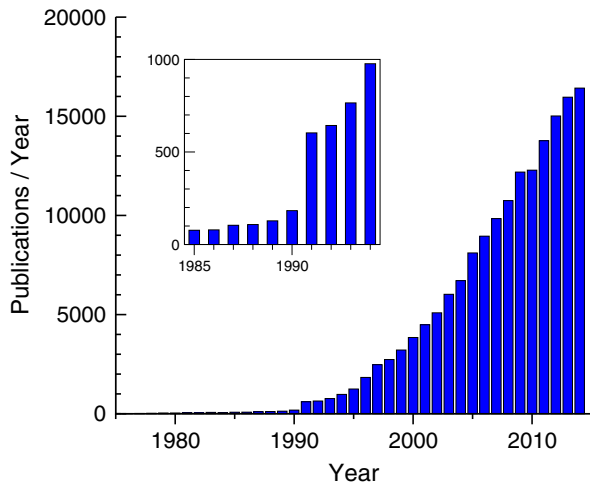
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The impact and challenge of DFT

- Density-functional theory is almost ubiquitous in quantum molecular & materials simulation.
- Of the 100 most cited papers in *any* field during 1900-2014, 12 pertain to DFT (2 are in the top 10). For details, see Nature 514, 550 (2014).

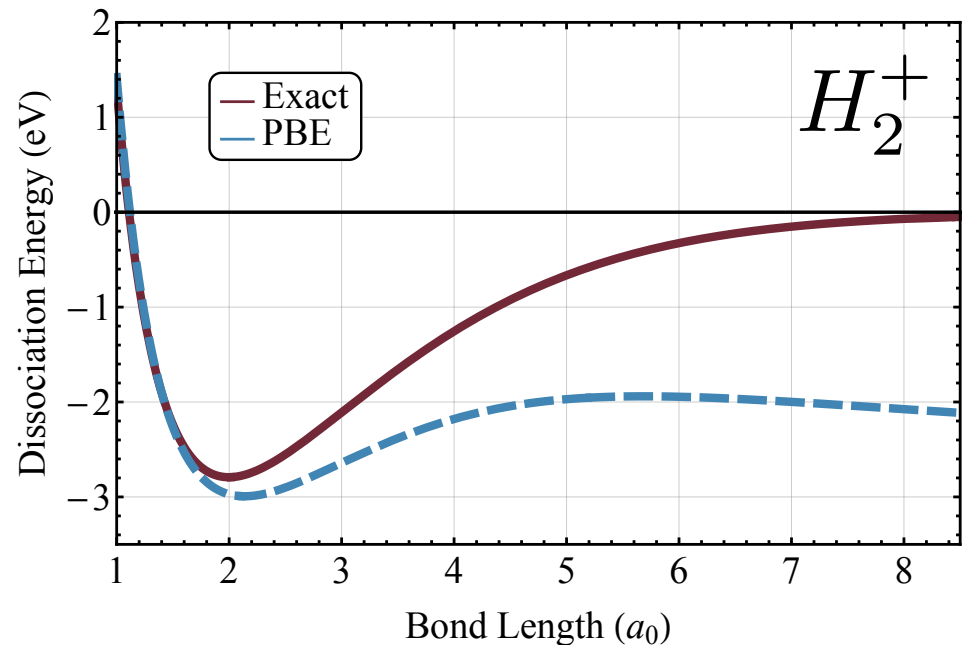
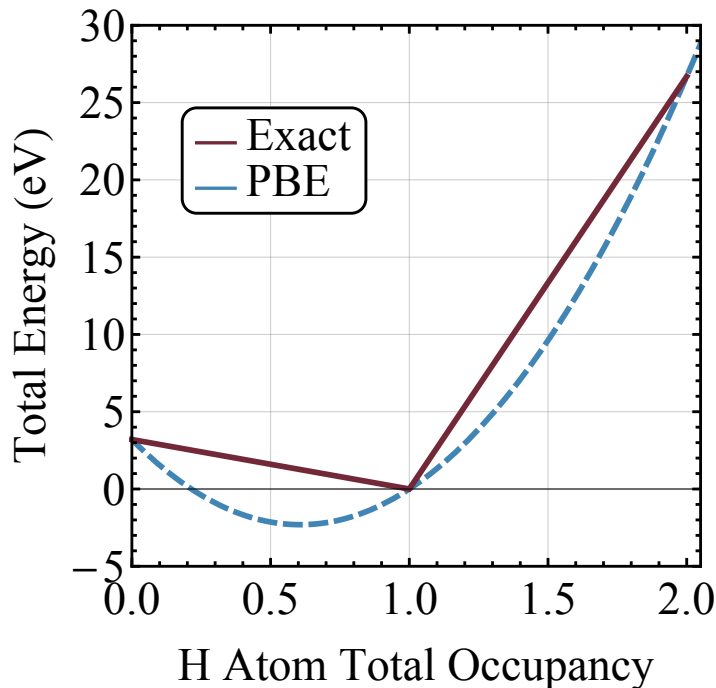


— R. O. Jones, Rev. Mod. Phys. **87**, 897 (2015).

— materialsproject.org (Lawrence Berkeley National Laboratory)

Systemic error #1: delocalisation error

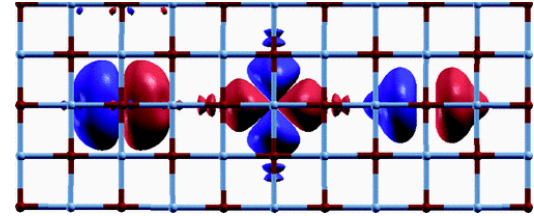
- A type of electron self-interaction error
- Insulating gap, polarisation, charge-transfer
- Magnetisation, ionisation potential, binding curves



- J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. 49, 1691 (1982)
- A. J. Cohen, P. Mori-Sanchez, and W. Yang, J. Chem. Phys. 129, 121104 (2008)
- A. J. Cohen, P. Mori-Sanchez, and W. Yang, Science 321, 792 (2008)

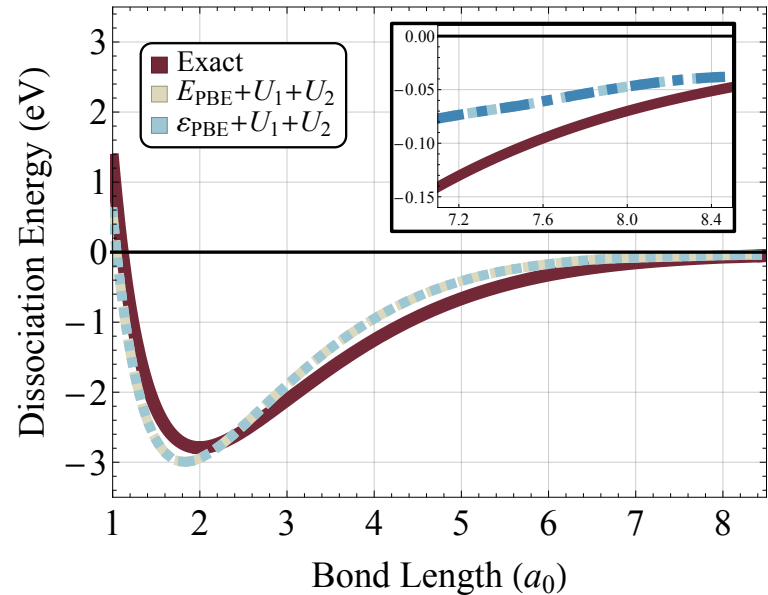
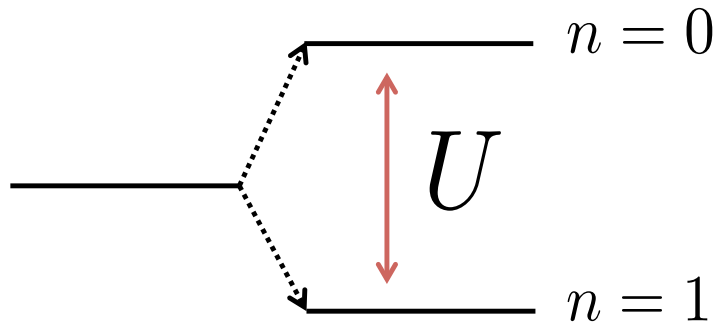
DFT+U : the modern interpretation

$$E_U = \sum_{I,\sigma} \frac{U}{2} \text{Tr}[\hat{n}^{I\sigma} - \hat{n}^{I\sigma} \hat{n}^{I\sigma}]$$



$$\hat{V}^{I\sigma} = \frac{U}{2} (1 - 2\hat{n}^{I\sigma})$$

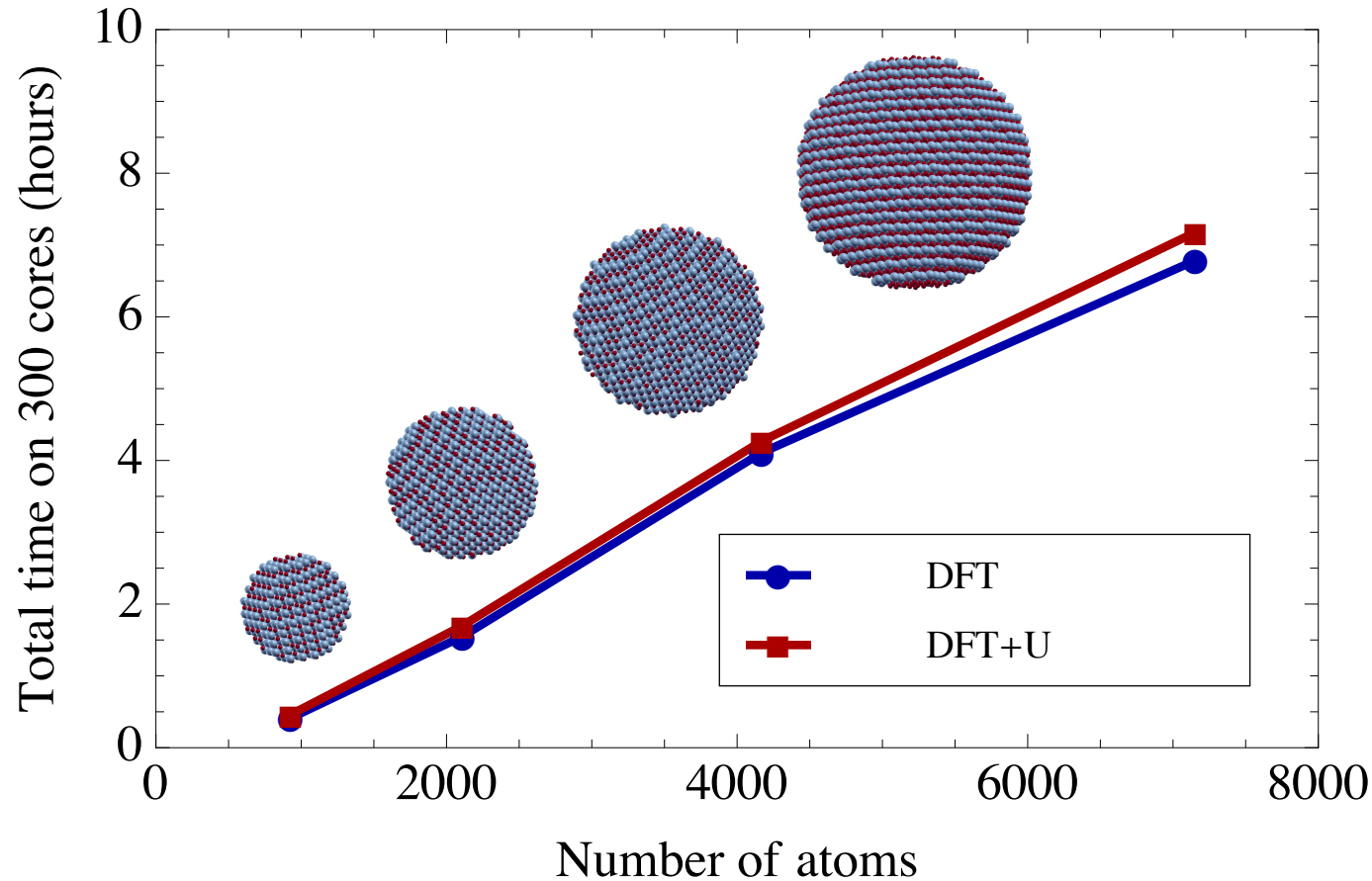
$$\hat{n}^{I\sigma} = \hat{P}^I \hat{\rho}^\sigma \hat{P}^I \quad \hat{P} = \sum |\varphi_m\rangle \langle \varphi_m|$$



- M. Cococcioni and S. de Gironcoli, Phys. Rev. B 71, 035105 (2005)
- W.E. Pickett, S.C. Erwin, E.C. Ethridge, Phys. Rev. B, 58, 1201 (1998)
- V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B 44, 943 (1991)
- A. J. Cohen, P. Mori-Sanchez, and W. Yang, Science 321, 792 (2008)

DFT+U₁+U₂ : Phys. Rev. B
94, 220104(R) (2016).

Algorithmic linear-scaling demonstration (NiO)



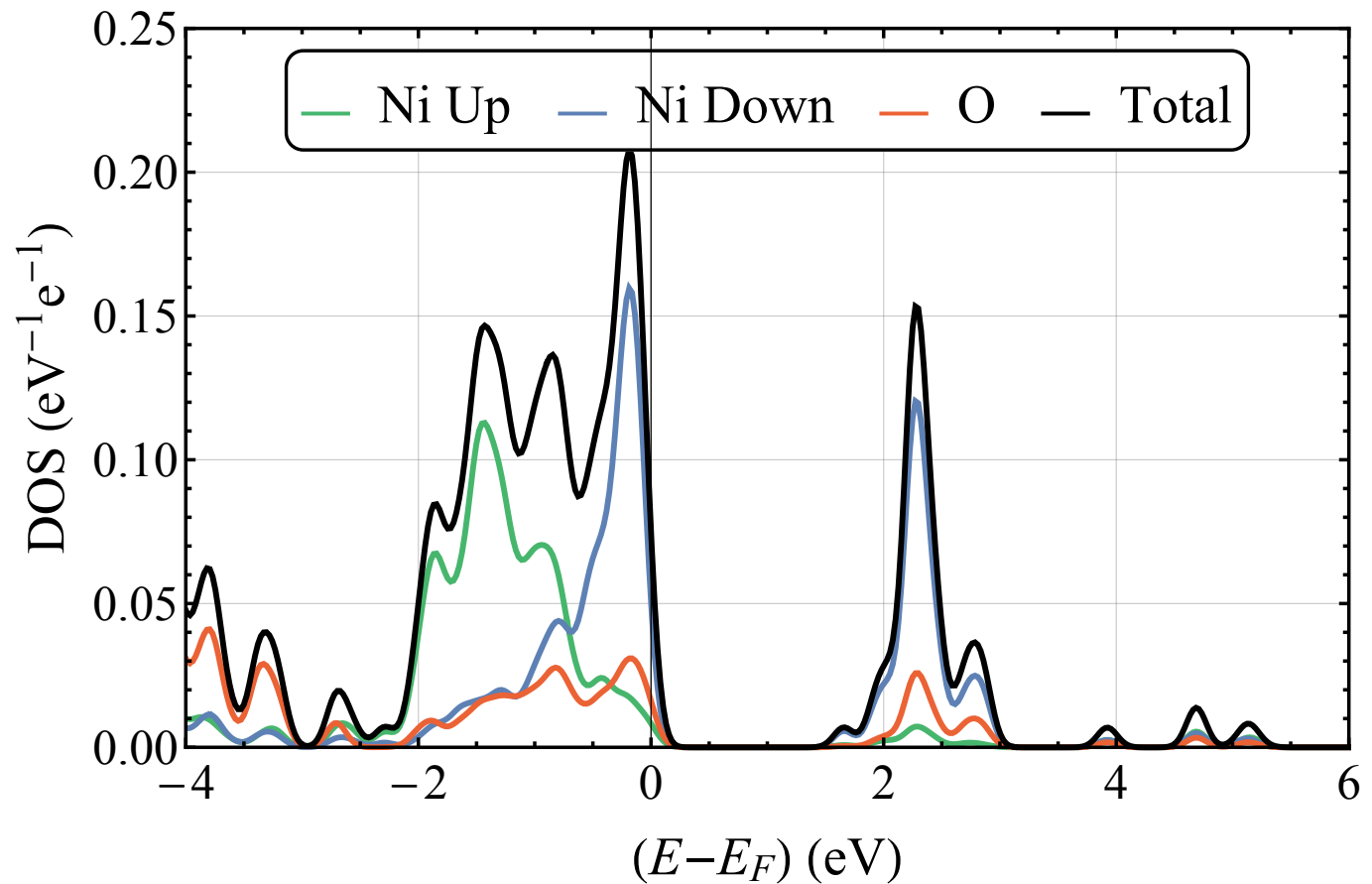
- Cite ONETEP DFT+U with: PRB 85, 085107 (2012) & PRB 83, 245124 (2011).
- Cite computed U or J in ONETEP with: Phys. Rev. B 98, 235157 (2018).
- To see a cool recent application: J. Phys. Chem. C 126 (43), 18439 (2022).

NiO DFT(PBE) DoS

Exp: Band gap = 3.0 eV Mag. Mom. = 1.6 – 1.9 μB

PBE: Band gap = 1.66 eV Mag. Mom. = 1.37 μB

$$U = 6.7 \text{ eV}$$



To turn on DFT+U (even just for popn. analysis)

- !! To set up anti-ferromagnetism and neutral projector orbitals for DFT+U.
- %BLOCK SPECIES_ATOMIC_SET
- Ni1 "SOLVE conf=3s2 3p6 3d8 4s2 4p0 SPIN=+2 CHARGE=+2"
- Ni2 "SOLVE conf=3s2 3p6 3d8 4s2 4p0 SPIN=-2 CHARGE=+2"
- O "SOLVE"
- %ENDBLOCK SPECIES_ATOMIC_SET

See the tutorial on how to calculate U and J

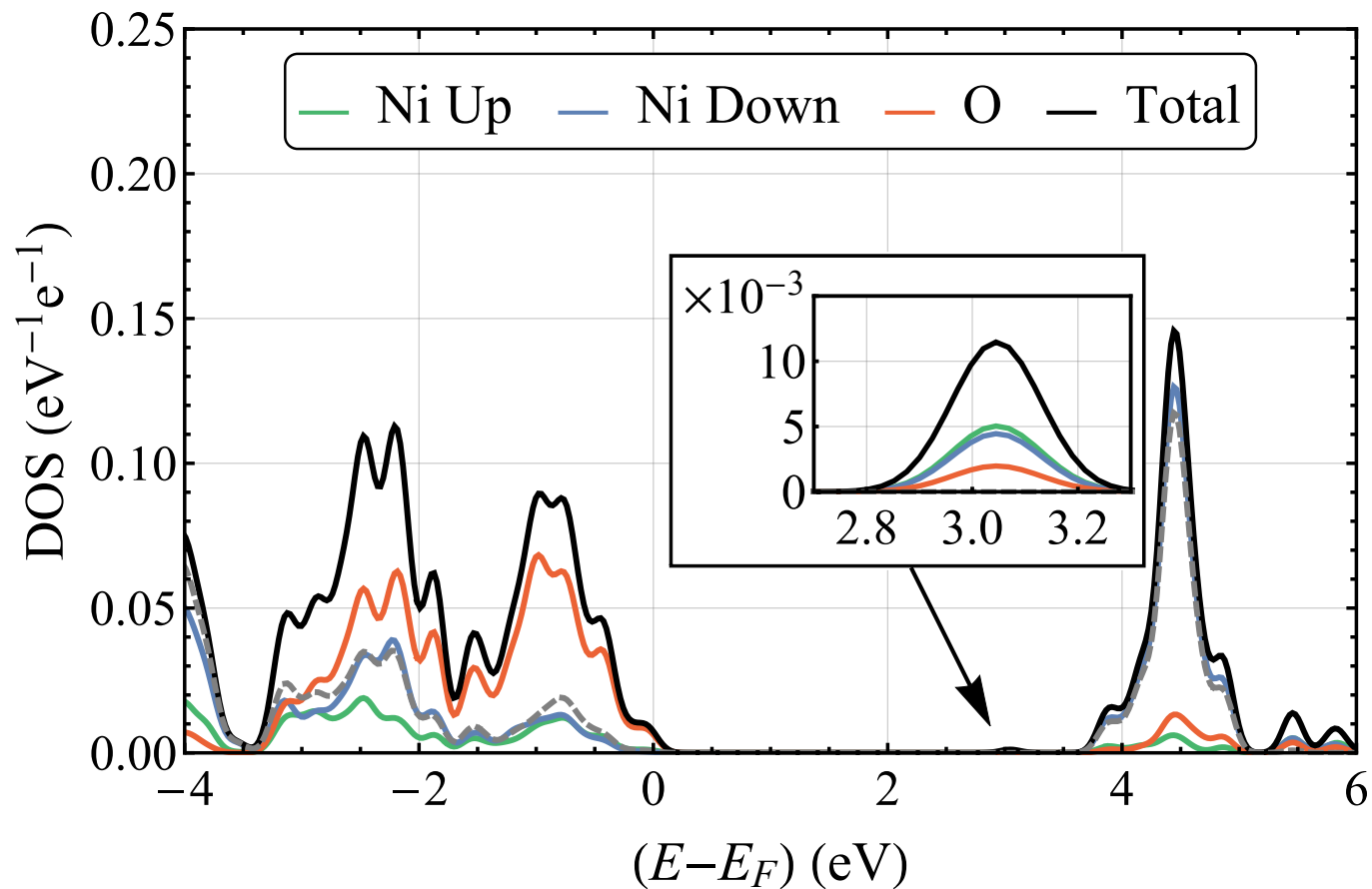
- !! Then to run DFT+U, in this case on Ni 3d orbitals only.
- %block hubbard
- Ni1 2 6.7 0.0 -10.0 0.0 0.0
- Ni2 2 6.7 0.0 -10.0 0.0 0.0
- %endblock hubbard

NiO DFT(PBE)+U DoS

Exp: Band gap = 3.0 eV Mag. Mom. = 1.6 – 1.9 μ_B

PBE+U: Band gap = 3.04 eV Mag. Mom. = 1.62 μ_B

➤ S. Hufner, Adv. Phys. 43, 183 (1994)



How to measure U (SIE) on sub-spaces?

- Define U as the subspace-averaged rate of change of Hxc potential on charge N, w.r.t. N.

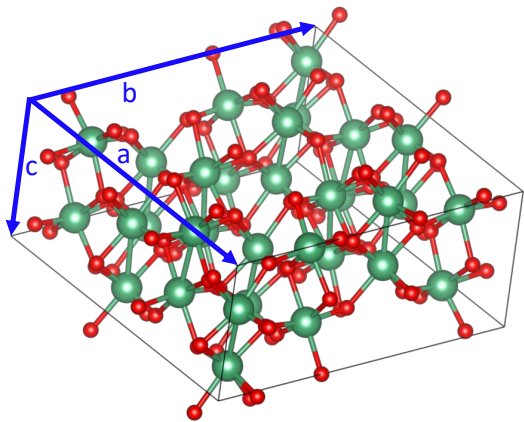
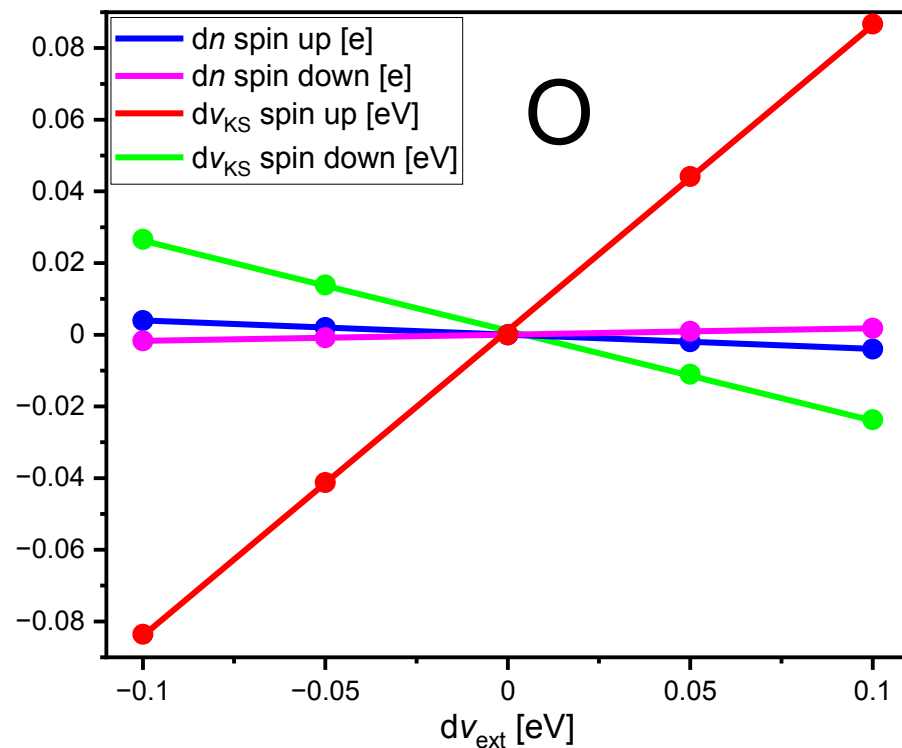
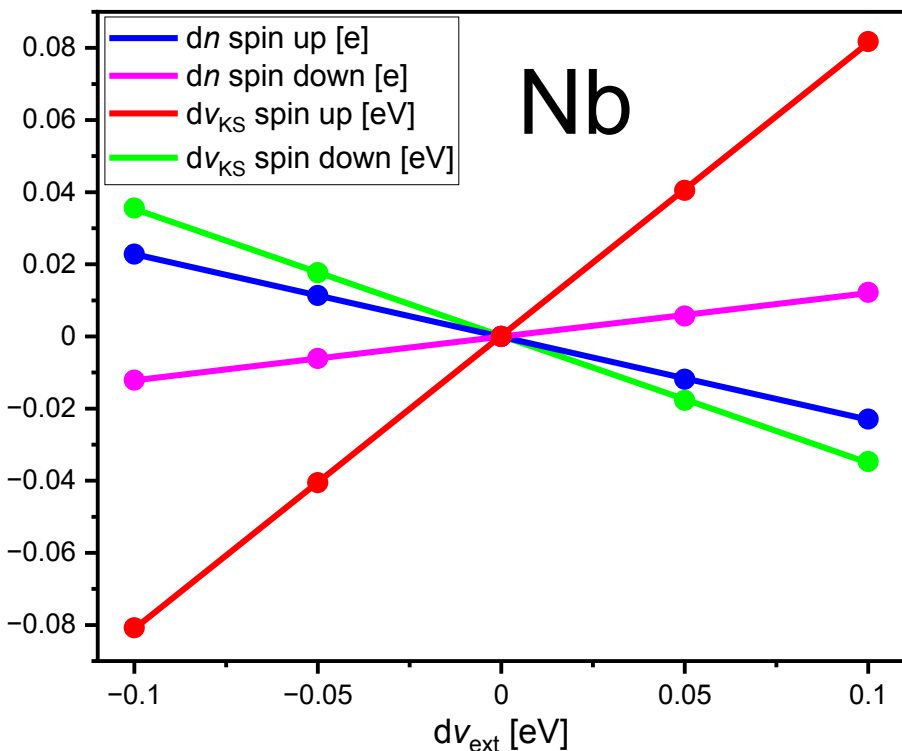
- If
$$N = \text{Tr} \left[(\rho^\uparrow + \rho^\downarrow) \hat{P} \right]$$

$$v^N = \text{Tr} \left[(v^\uparrow + v^\downarrow) \hat{P} \right] / 2 \text{Tr} \left[\hat{P} \right]$$

- then
$$U \equiv \frac{dv_{\text{Hxc}}^N}{dN} = \chi_{N0}^{-1} - \chi_N^{-1}$$

- where
$$\chi_{N0}^{-1} = \frac{dv_{\text{KS}}^N}{dN}, \quad \chi_N^{-1} = \frac{dv_{\text{ext}}^N}{dN} = \frac{d\alpha}{dN}$$

Computing U and J in ONETEP (example: NbO₂)



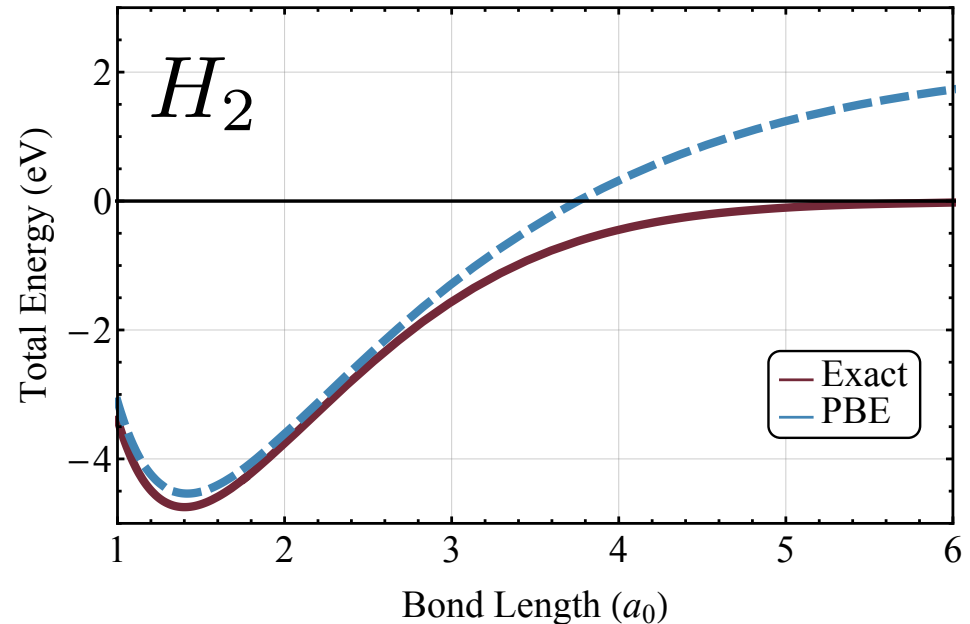
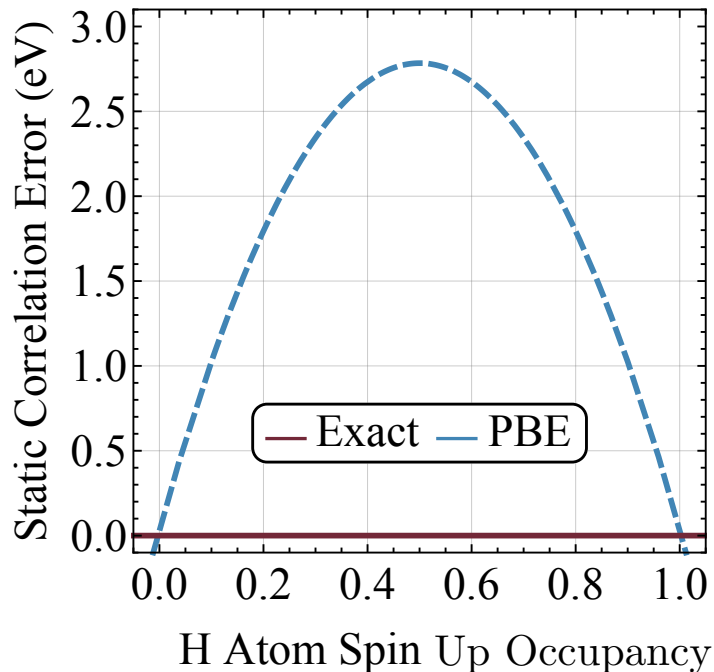
	Niobium	Oxygen
U	2.48	9.02
J	0.23	0.90
$U_{\text{eff}} = U - J$	2.25	8.12
$U_{\text{full}} = U - 2J$	2.02	7.22

Systemic error #2: static correlation error

$$E \left[\sum_{i=1}^g c_i \rho_i \right] = E [\rho_j]$$

For g degenerate states:

$$j = \{1, \dots, g\} \quad \sum_{i=1}^g c_i = 1$$



- J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. 49, 1691 (1982)
- A. J. Cohen, P. Mori-Sanchez, and W. Yang, J. Chem. Phys. 129, 121104 (2008)
- A. J. Cohen, P. Mori-Sanchez, and W. Yang, Science 321, 792 (2008)

How to quantify J (SCE) on sub-spaces?

- Define J as minus the subspace-averaged rate of change of Hxc potential on magnetism M, w.r.t. M.

- If
$$M = \text{Tr} \left[(\rho^\uparrow - \rho^\downarrow) \hat{P} \right]$$
$$v^M = \text{Tr} \left[(v^\uparrow - v^\downarrow) \hat{P} \right] / 2 \text{Tr} \left[\hat{P} \right]$$

- then
$$-J \equiv \frac{dv_{\text{Hxc}}^M}{dM} = \chi_{M0}^{-1} - \chi_M^{-1}$$

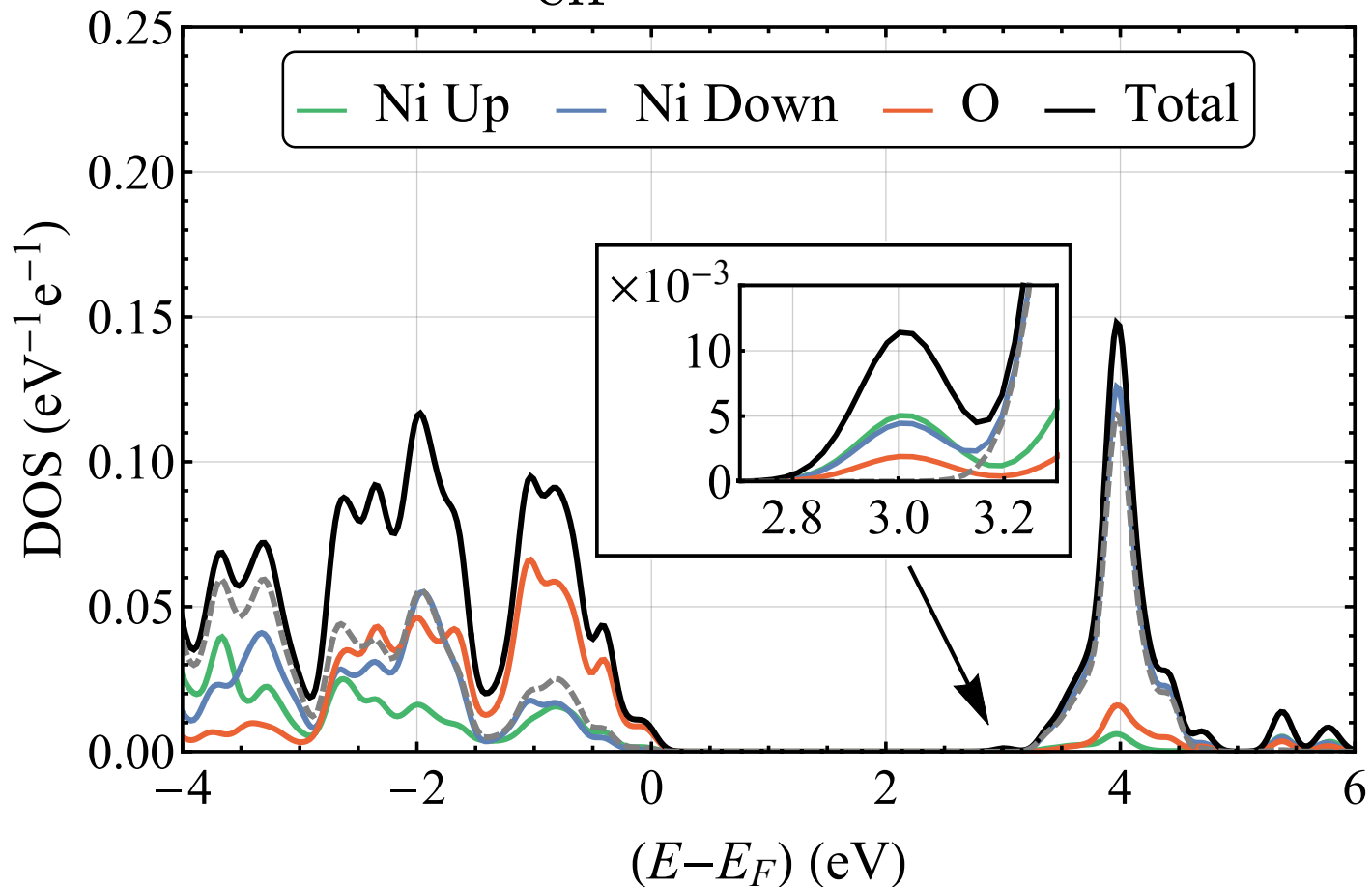
- where
$$\chi_{M0}^{-1} = \frac{dv_{\text{KS}}^M}{dM}, \quad \chi_M^{-1} = \frac{dv_{\text{ext}}^M}{dM} = \frac{d\beta}{dM}$$

NiO self-consistent DFT(PBE)+(U-J) DoS

Exp: Band gap = 3.0 eV Mag. Mom. = 1.6 – 1.9 μB

PBE+U: Band gap = 3.0 eV Mag. Mom. = 1.57 μB

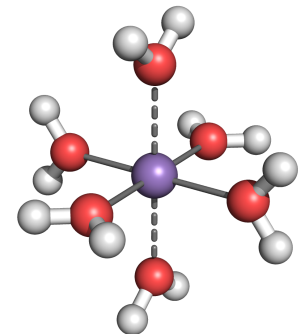
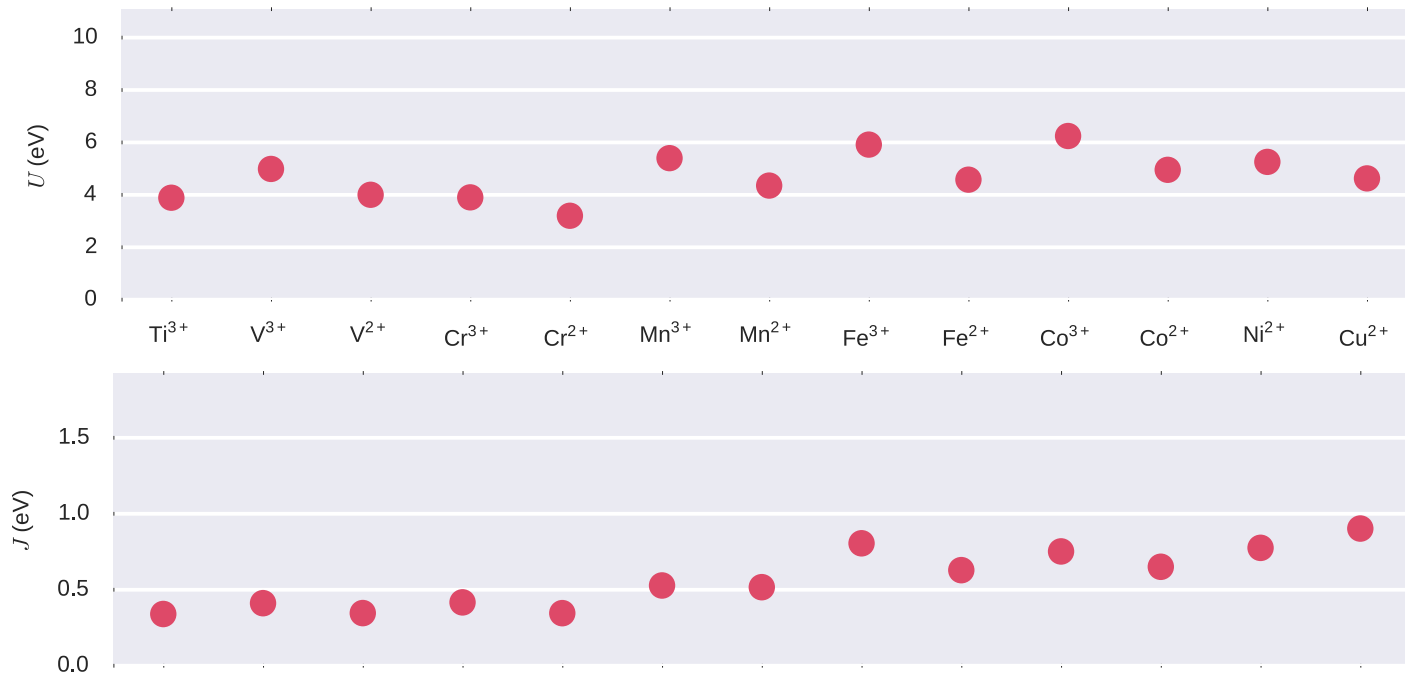
$$U_{\text{eff}} = 5.2 \text{ eV}$$



Hund's J for static correlation error

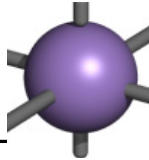

- The analogue of the Hubbard U for the static correlation error is Hund's J, which we define as:

$$J = -\frac{1}{2} \frac{d(v_{\text{Hxc}}^{\uparrow} - v_{\text{Hxc}}^{\downarrow})}{d(n^{\uparrow} - n^{\downarrow})} \quad U = \frac{1}{2} \frac{d(v_{\text{Hxc}}^{\uparrow} + v_{\text{Hxc}}^{\downarrow})}{d(n^{\uparrow} + n^{\downarrow})}$$



Are only TM 3d orbitals error-prone?

- Oxygen 2p orbitals often harbour large U values.

Metal	U		J	U		J
Ti ³⁺	3.89 ± 0.01		0.34 ± 0.00	8.13 ± 0.02		1.05 ± 0.00
V ²⁺	4.00 ± 0.01		0.35 ± 0.00	8.28 ± 0.01		1.29 ± 0.00
Cr ³⁺	3.90 ± 0.01		0.42 ± 0.00	8.29 ± 0.02		1.08 ± 0.01
Cr ²⁺	3.20 ± 0.01		0.35 ± 0.00	8.45 ± 0.02		1.27 ± 0.01
Mn ³⁺	5.40 ± 0.01		0.53 ± 0.00	8.57 ± 0.03		0.97 ± 0.01
Mn ²⁺	4.35 ± 0.01		0.52 ± 0.01	8.31 ± 0.01		1.30 ± 0.01
Fe ³⁺	5.92 ± 0.02		0.81 ± 0.02	8.40 ± 0.12		1.06 ± 0.06
Fe ²⁺	4.58 ± 0.01		0.63 ± 0.01	8.83 ± 0.01		1.39 ± 0.01
Co ³⁺	6.25 ± 0.00		0.75 ± 0.00	8.39 ± 0.10		1.12 ± 0.05
Co ²⁺	4.96 ± 0.02		0.65 ± 0.01	8.25 ± 0.09		1.37 ± 0.06
Ni ²⁺	5.26 ± 0.01		0.78 ± 0.01	8.09 ± 0.01		1.37 ± 0.00
Cu ²⁺	4.63 ± 0.01		0.90 ± 0.01	8.38 ± 0.01		1.38 ± 0.00
MnO	5.37 ± 0.04		0.49 ± 0.02	10.92 ± 0.12		1.03 ± 0.03

DFT+U+J: the second easiest way to include J

- See Phys. Rev. B **84**, 115108 (2011) for derivation.

$$E_{U+J} = \sum_{I,\sigma} \frac{U - J}{2} \text{Tr} [\hat{n}^{I\sigma} - \hat{n}^{I\sigma} \hat{n}^{I\sigma}] + \frac{J}{2} \text{Tr} [\hat{n}^{I\sigma} \hat{n}^{I\bar{\sigma}}]$$

$$\hat{v}_{U+J}^{I\sigma} = \frac{U - J}{2} \left(\hat{P} - 2\hat{n}^{I\sigma} \right) + J\hat{n}^{I\bar{\sigma}}$$

- In closed-shell systems, the gap goes like $U - 2J$:

$$\hat{v}_{U+J}^{I\sigma} = \frac{U - 2J}{2} \left(\hat{P} - 2\hat{n}^{I\sigma} \right) + \frac{J}{2} \hat{P}$$

- There, also symmetry allows U and J to be calculated simultaneously with one set of perturbations, e.g. applied to spin-up only. See Phys. Rev. B **101**, 245137 (2020).

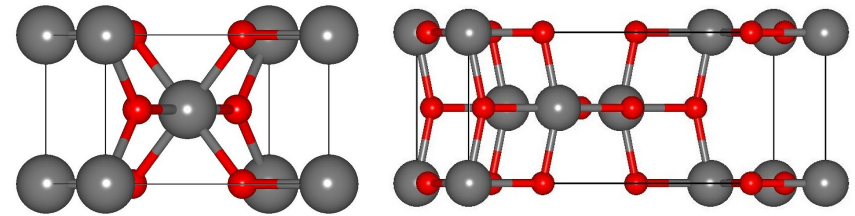
DFT(LDA)+U+J density of states for TiO₂

TiO ₂ -rutile E_{gap}		
DFT (LDA)	1.96	
	U^d	$U^{d,p}$
DFT+U	2.24	3.59
DFT+ $U_{\text{eff}} = U - J$	2.21	3.38
DFT+ $U_{\text{full}} = U - 2J, \alpha = -J/2$	2.17	3.32
DFT+ $U_{\text{full}} = U - 2J$	2.18	3.18
DFT+ $U_{\text{full}} = U - 2J, \alpha = J/2$	2.20	3.04
DFT+U+J (no minority spin term)	2.20	3.04
Experiment [12, 13]		3.03
LDA [48]		1.79
PBE [19]		1.88
PBE [75]		1.86
PBE [76]		1.77
TB-mBJ [77]		2.60
SCAN [78]		2.23
HSE06 [79]		3.3
HSE06 [19]		3.39
HSE06 ($\alpha = 0.2$) [76]		3.05
sX Hybrid [75]		3.1
LDA+G ₀ W ₀ [18]		3.34
PBE+G ₀ W ₀ [19]		3.46
HSE+G ₀ W ₀ [19]		3.73
DFT+U ($U=7.5$ eV) [80]		2.83
DFT+U ($U=10$ eV) [81]		2.97
DFT+ U^d ($U = 3.25$ eV) [82]		2.01
DFT+ $U^{d,p}$ ($U^d = 3.25$ eV, $U^p = 10.65$ eV) [82]		3.67
DFT+ $U^{d,p}$ ($U^d = 3.25$ eV, $U^p = 5.0$ eV) [82]		2.69
DFT+ $U^{d,p}$ ($U^d = 0.15$ eV, $U^p = 7.34$ eV) [83]		2.83

— Lessons learned:
 O 2p correction is needed;
 smooth neutral orbitals seem best;
 the DFT+U+J potential seems good.

DFT(LDA)+U+J density of states for TiO₂

TiO ₂ -anatase E_{gap}		
DFT (LDA)	2.21	
	$+U^d$	$+U^{d,p}$
DFT+ U	2.51	4.13
DFT+ $U_{\text{eff}} = U - J$	2.48	3.88
DFT+ $U_{\text{full}} = U - 2J, \alpha = -J/2$	2.41	3.81
DFT+ $U_{\text{full}} = U - 2J$	2.45	3.65
DFT+ $U_{\text{full}} = U - 2J, \alpha = J/2$	2.49	3.50
DFT+ $U+J$ (no minority spin term)	2.49	3.50
Experiment [11]	3.47	
PBE [19]	1.94	
TB-mBJ [77]	3.01	
SCAN [78]	2.56	
HSE06 [19, 79]	3.60	
LDA+G ₀ W ₀ [18]	3.56	
PBE+G ₀ W ₀ [11]	3.61	
PBE+G ₀ W ₀ [19]	3.73	
HSE+G ₀ W ₀ [19]	4.05	
DFT+ U^d ($U=7.5$ eV) [80]	3.27	
DFT+ U^d ($U = 3.23$ eV) [82]	2.43	
DFT+ $U^{d,p}$ ($U^d = 3.23$ eV, $U^p = 10.59$ eV) [82]	4.24	
DFT+ $U^{d,p}$ ($U^d = 3.23$ eV, $U^p = 5.0$ eV) [82]	3.23	



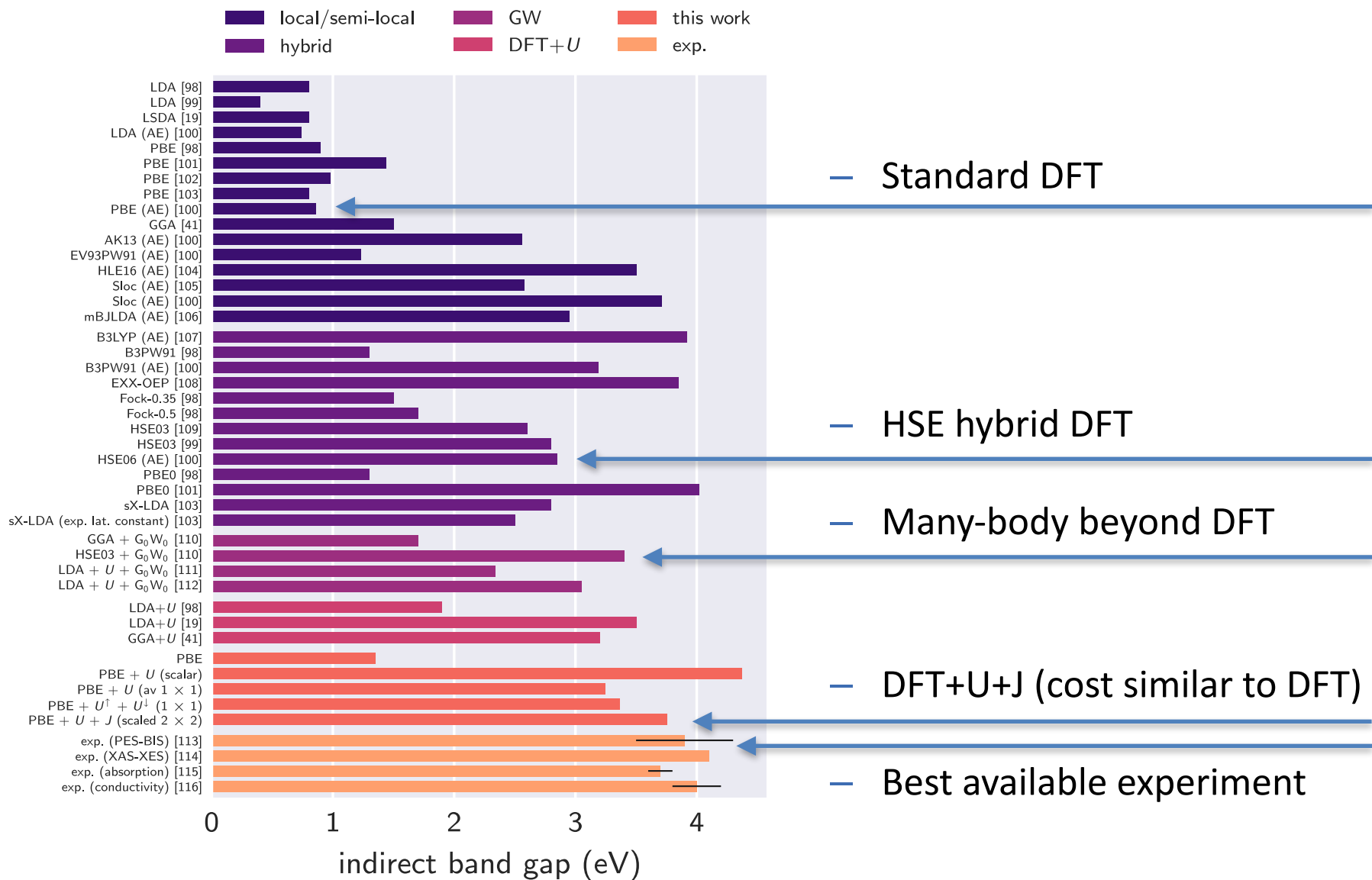
(a) Rutile

(b) Anatase

TiO ₂ -rutile E_{gap}				
Subspace definition	Ti ⁰		Ti ³⁺	
	1.96		1.96	
DFT(LDA)	$+U^d$	$+U^{d,p}$	$+U^d$	$+U^{d,p}$
U	2.24	3.59	2.69	4.20
$U_{\text{eff}} = U - J$	2.21	3.38	2.63	3.94
$U_{\text{full}} = U - 2J, \alpha = -J/2$	2.17	3.32	2.52	3.81
$U_{\text{full}} = U - 2J$ from Ti ⁰	2.18	3.18	2.31	3.33
$U_{\text{full}} = U - 2J$ from Ti ³⁺	2.38	3.46	2.57	3.69
$U_{\text{full}} = U - 2J, \alpha = J/2$	2.20	3.04	2.62	3.58
$U+J$ (no minority spin term)	2.20	3.04	2.64	3.58

- Lessons learned:
The arbitrariness with respect to orbital choice does not go away.
- Again O 2p correction restores the lattice.

MnO: a near 'worst case' scenario test



ONETEP as engine for functional development

- BLOR is an exactified DFT+U functional based on idea of measuring and correcting self-interaction and static correlation error in situ. For single-orbital subspaces, it can be shown to be unique, and it differs from conventional DFT+U+J.

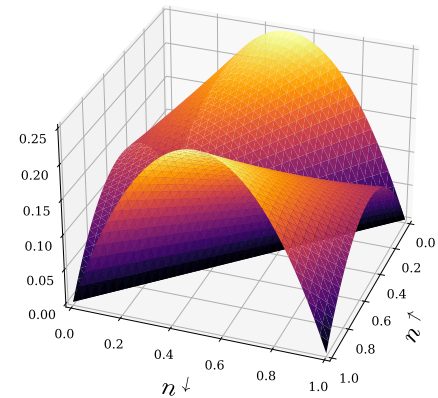
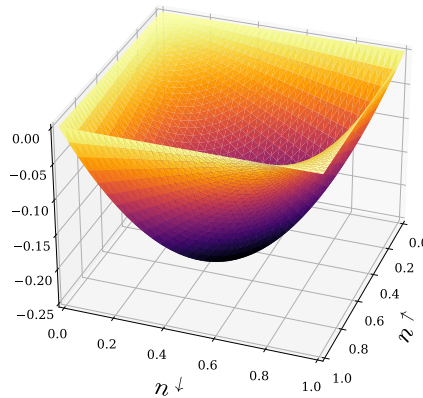
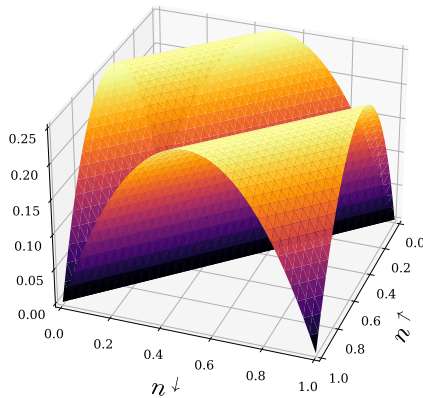
$$E_{\text{BLOR}} = \begin{cases} \frac{U^\uparrow + U^\downarrow}{4} \text{Tr}[\hat{N} - \hat{N}^2] + \frac{J}{2} \text{Tr}[\hat{M}^2 - \hat{N}^2] + \frac{U^\uparrow - U^\downarrow}{4} \text{Tr}[\hat{M} - \hat{N}\hat{M}], & \text{Tr}[\hat{N}] \leq \text{Tr}[\hat{P}]. \\ \underbrace{\frac{U^\uparrow + U^\downarrow}{4} \text{Tr}[(\hat{N} - \hat{P}) - (\hat{N} - \hat{P})^2]}_{\text{Symmetric-MSIE term}} + \underbrace{\frac{J}{2} \text{Tr}[\hat{M}^2 - (\hat{N} - 2\hat{P})^2]}_{\text{SCE term}} + \underbrace{\frac{U^\uparrow - U^\downarrow}{4} \text{Tr}[\hat{M} - \hat{N}\hat{M}]}_{\text{Asymmetric-MSIE term}}, & \text{Tr}[\hat{N}] > \text{Tr}[\hat{P}]. \end{cases}$$

$$\hat{P} = \sum_m |\phi_m\rangle \langle \phi^m|$$

$$\hat{n}^\sigma = \hat{P} \hat{\rho}^\sigma \hat{P}$$

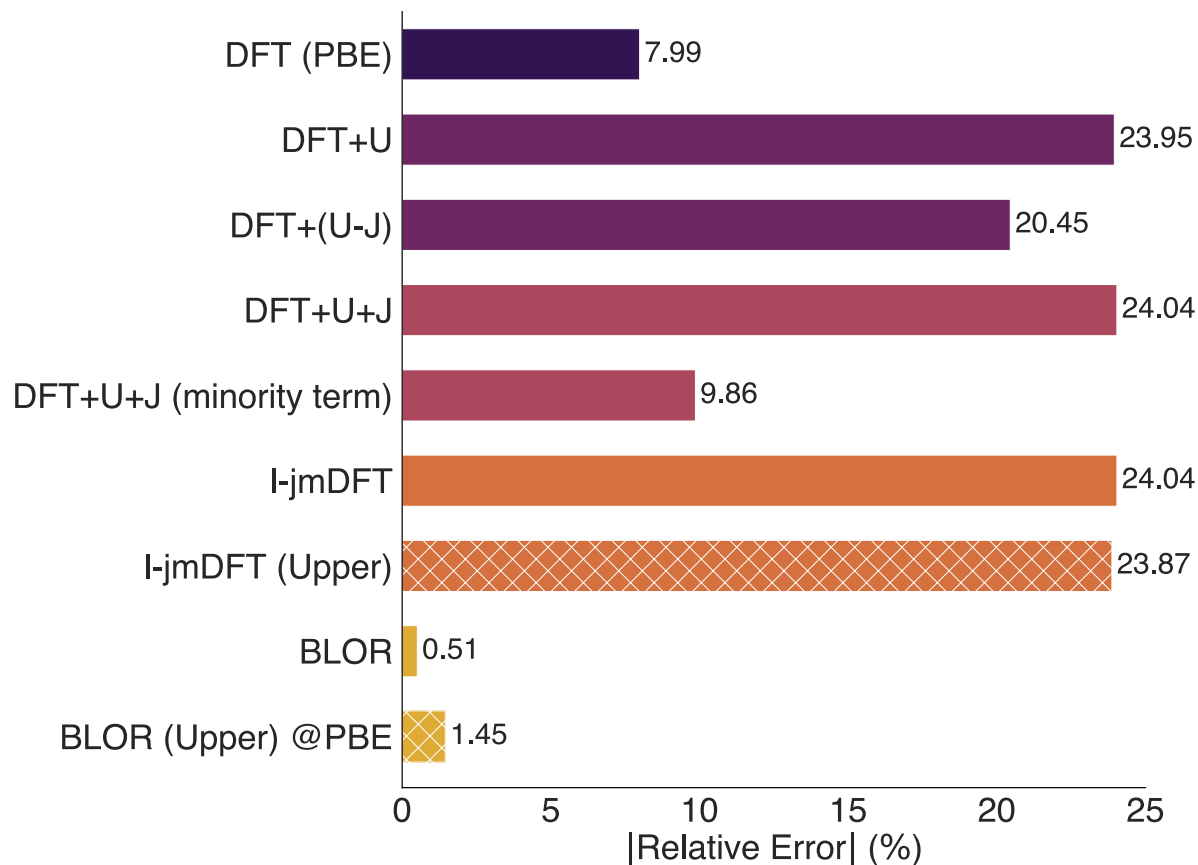
$$\hat{N} = \hat{n}^\uparrow + \hat{n}^\downarrow$$

$$\hat{M} = \hat{n}^\uparrow - \hat{n}^\downarrow$$



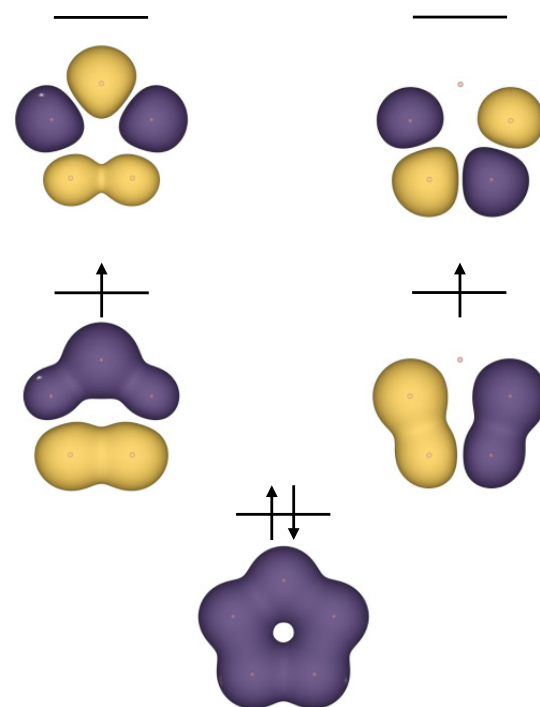
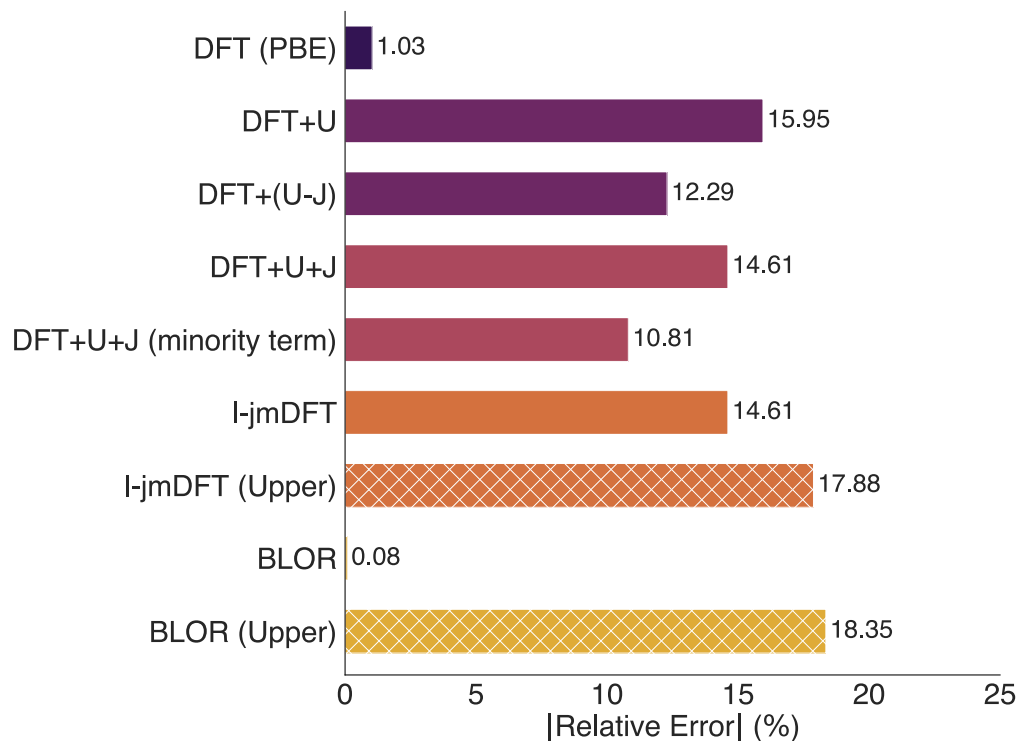
Test at near-maximal per-electron correlation

Dissociated H₂ Test System



Test case where all static errors are active

Dissociated Triplet H_5^+ Test System



- A. C. Burgess, E. Linscott, and D. D. O'Regan, Phys. Rev. B 107, L121115 (2023).
- A. C. Burgess and D. D. O'Regan, arXiv:2408.08391 (2024).



Trinity College Dublin

Coláiste na Tríonóide, Baile Átha Cliath

The University of Dublin

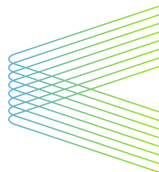
Thank you for listening

Chat here or contact for any DFT+U or general correlated electron support at:

- David.O.Regan@tcd.ie
- [@OREganGroupTCD](https://twitter.com/OREganGroupTCD)
- www.theoryofmaterials.com



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