Trinity College Dublin
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DFT+U+J and constrained DFT in ONETEP

How to teach DFT to self-correct and self-excite

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ONETEP Masterclass 2023

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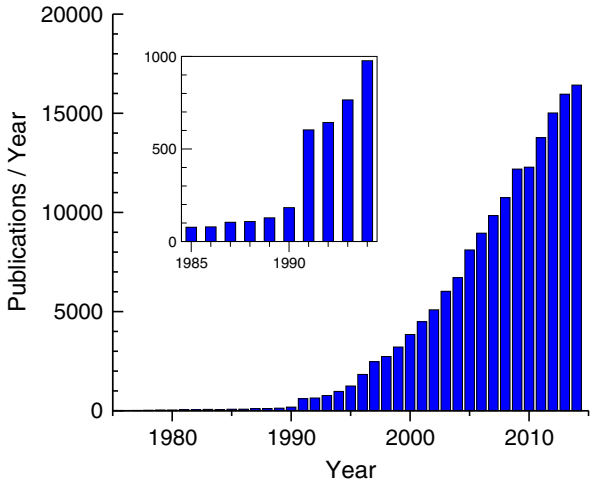
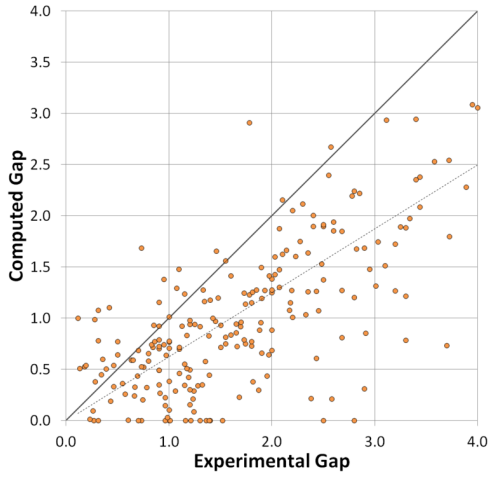
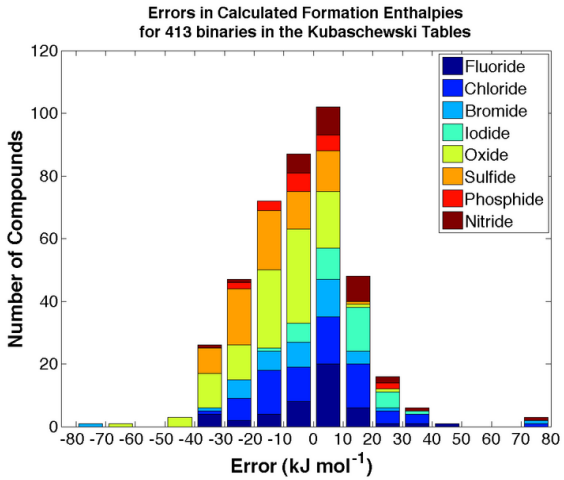
The impact and challenge of DFT

- 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).





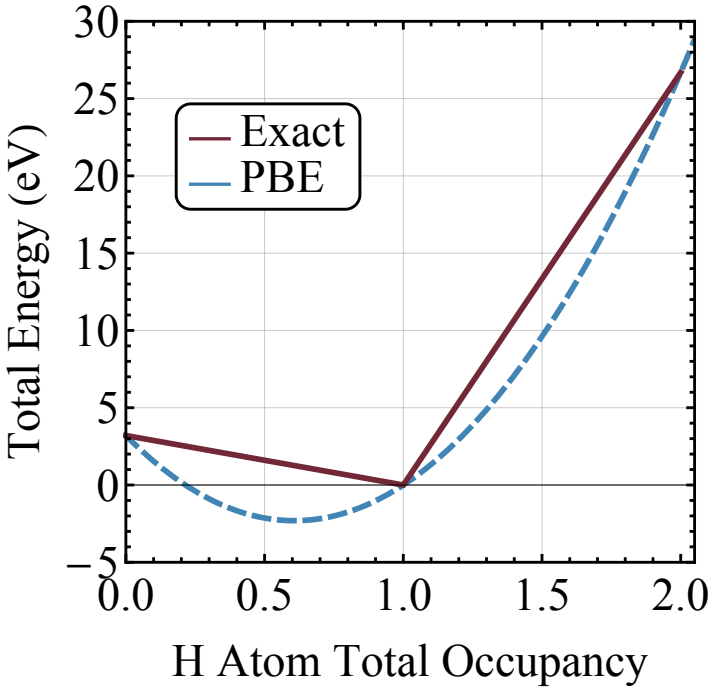


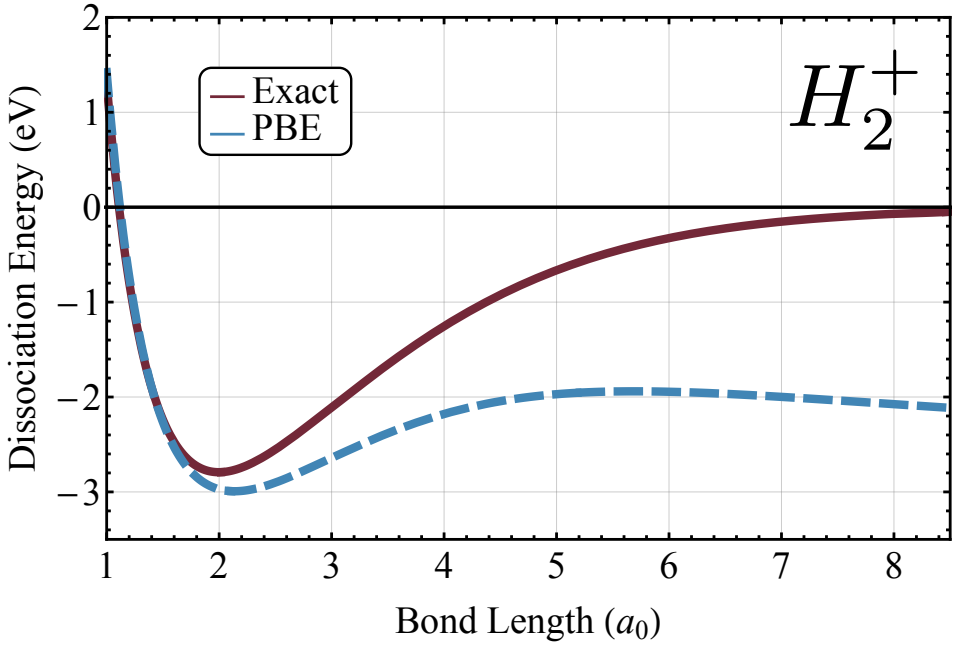
– R. O. Jones, Rev. Mod. Phys. **87**, 897 (2015).

– 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

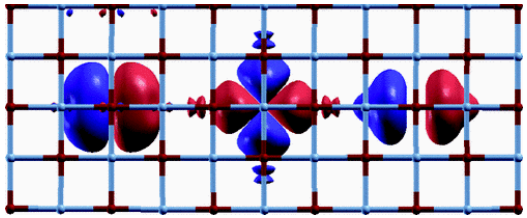




- J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. 49, 1691 (1982)
- A.J.Cohen,P.Mori-Sanchez,andW.Yang, J. Chem. Phys. 129, 121104 (2008)
- A. J. Cohen, P. Mori-Sanchez, and W. Yang, Science 321, 792 (2008)

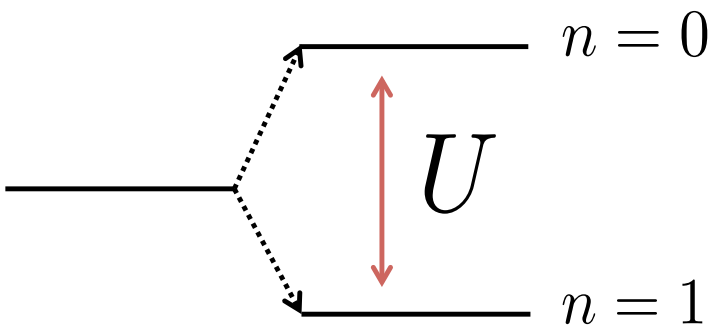
DFT+U : the modern interpretation

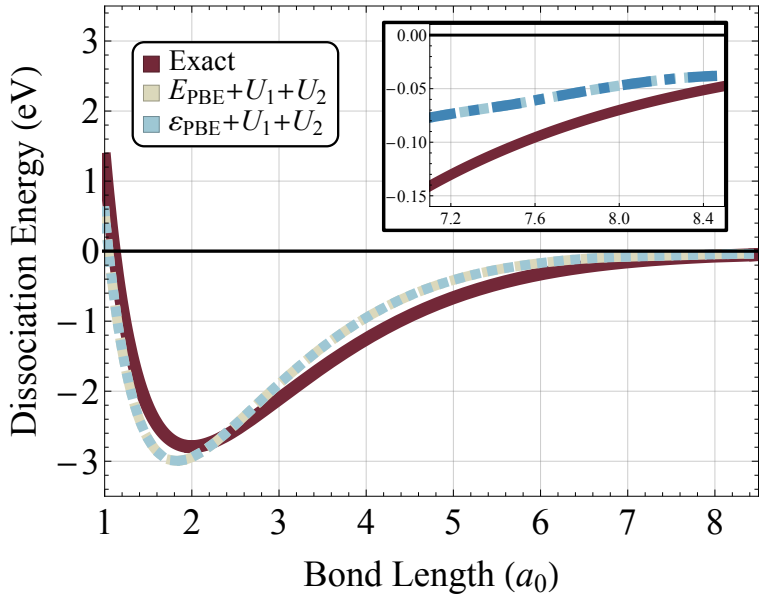
$$E_U = \sum_{I,\sigma} \frac{U}{2} \mathrm{Tr}[\hat{n}^{I\sigma} - \hat{n}^{I\sigma}\hat{n}^{I\sigma}]$$



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

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





- 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+U_1+U_2 : Phys. Rev. B **94**, 220104(R) (2016).

How to quantify SIE on sub-spaces?

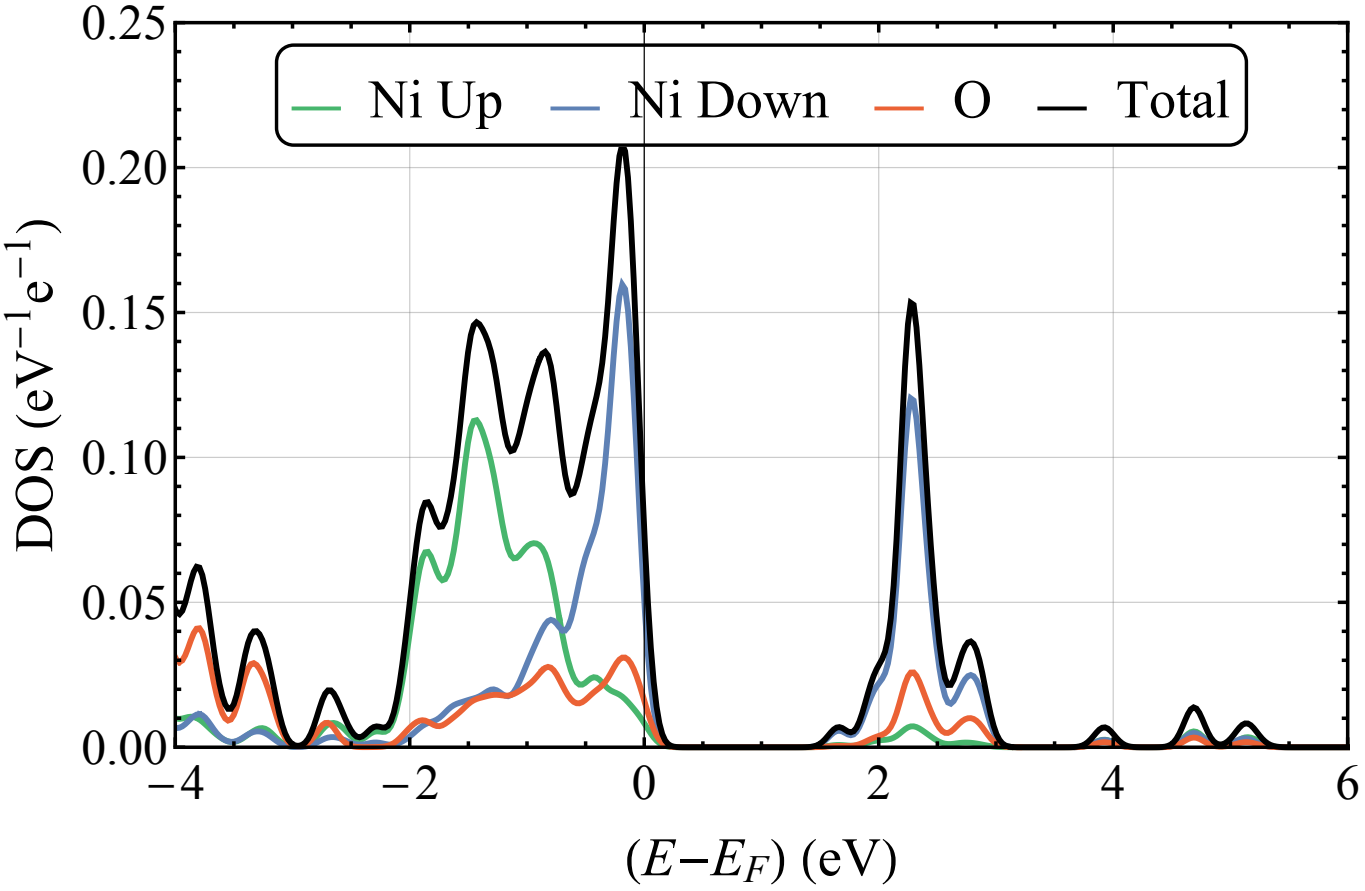
- Define U as the subspace-averaged rate of change of Hxc potential on charge N, w.r.t. N.
- If $$N = \mathrm{Tr}\left[\left(\rho^{\uparrow} + \rho^{\downarrow}\right)\hat{\mathrm{P}}\right]$$
$$v^{N} = \mathrm{Tr}\left[\left(\mathrm{v}^{\uparrow} + \mathrm{v}^{\downarrow}\right)\hat{\mathrm{P}}\right] / 2\mathrm{Tr}\left[\hat{\mathrm{P}}\right]$$
- then $$U \equiv \frac{dv^{N}_{\mathrm{Hxc}}}{dN} = \chi^{-1}_{N0} - \chi^{-1}_{N}$$
- where $$\chi^{-1}_{N0} = \frac{dv^{N}_{\mathrm{KS}}}{dN}, \quad \chi^{-1}_{N} = \frac{dv^{N}_{\mathrm{ext}}}{dN} = \frac{d\alpha}{dN}$$

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

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

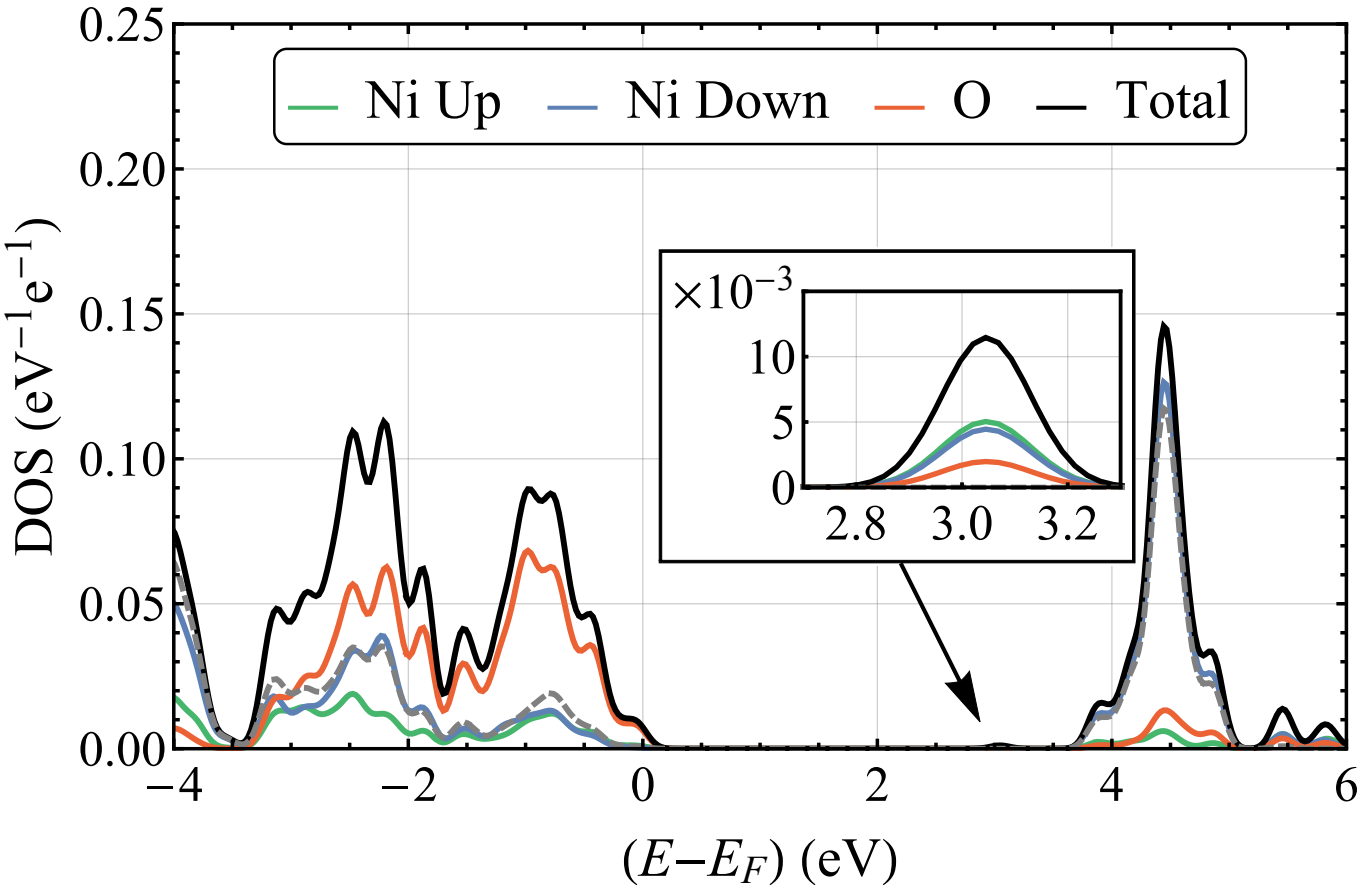


NiO DFT(PBE)+U DoS

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

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

- S. Hüfner, Adv. Phys. **43**, 183 (1994)

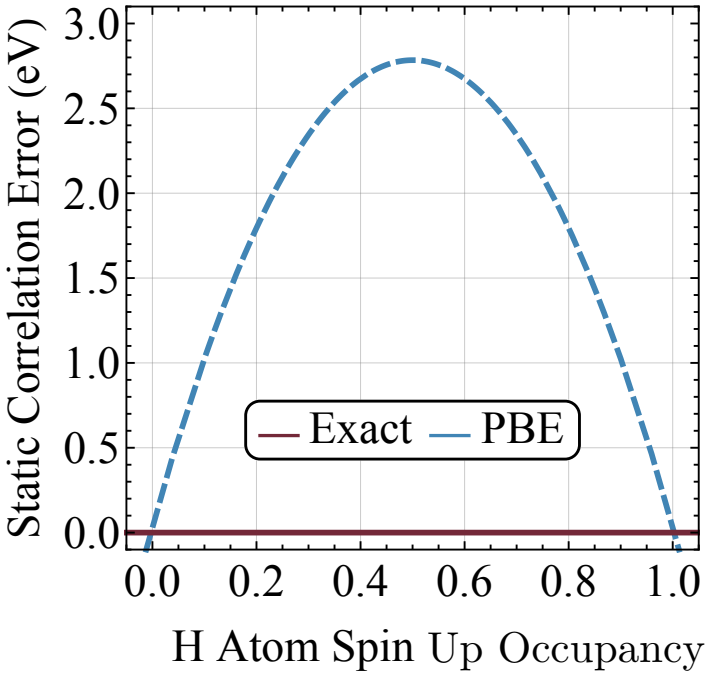


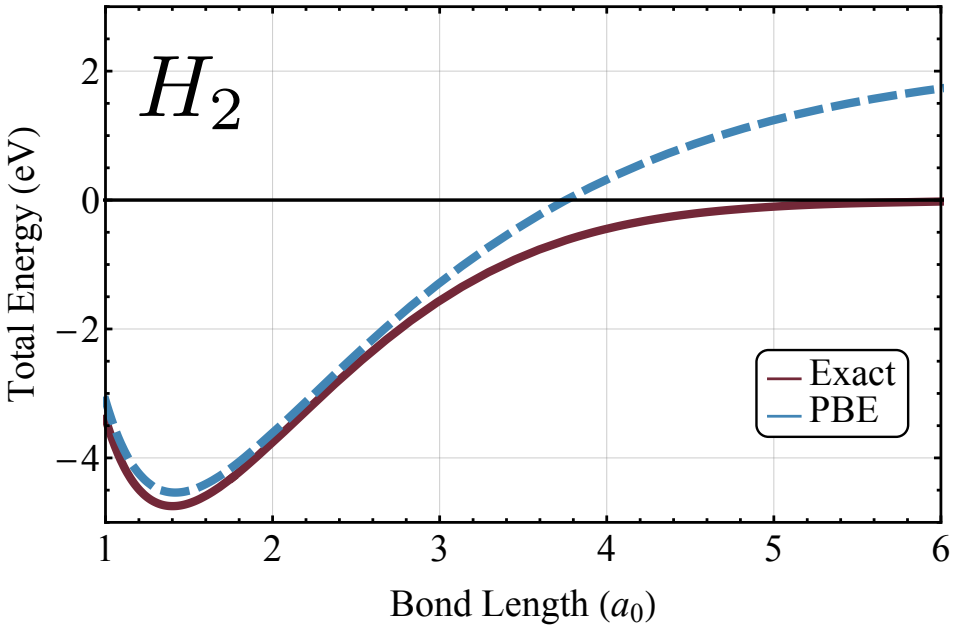
Systemic error #2: static correlation error

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

For g degenerate states:

$$j = \{1, \ldots, g\} \qquad \sum_{i=1}^{g} c_i = 1$$





- 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)

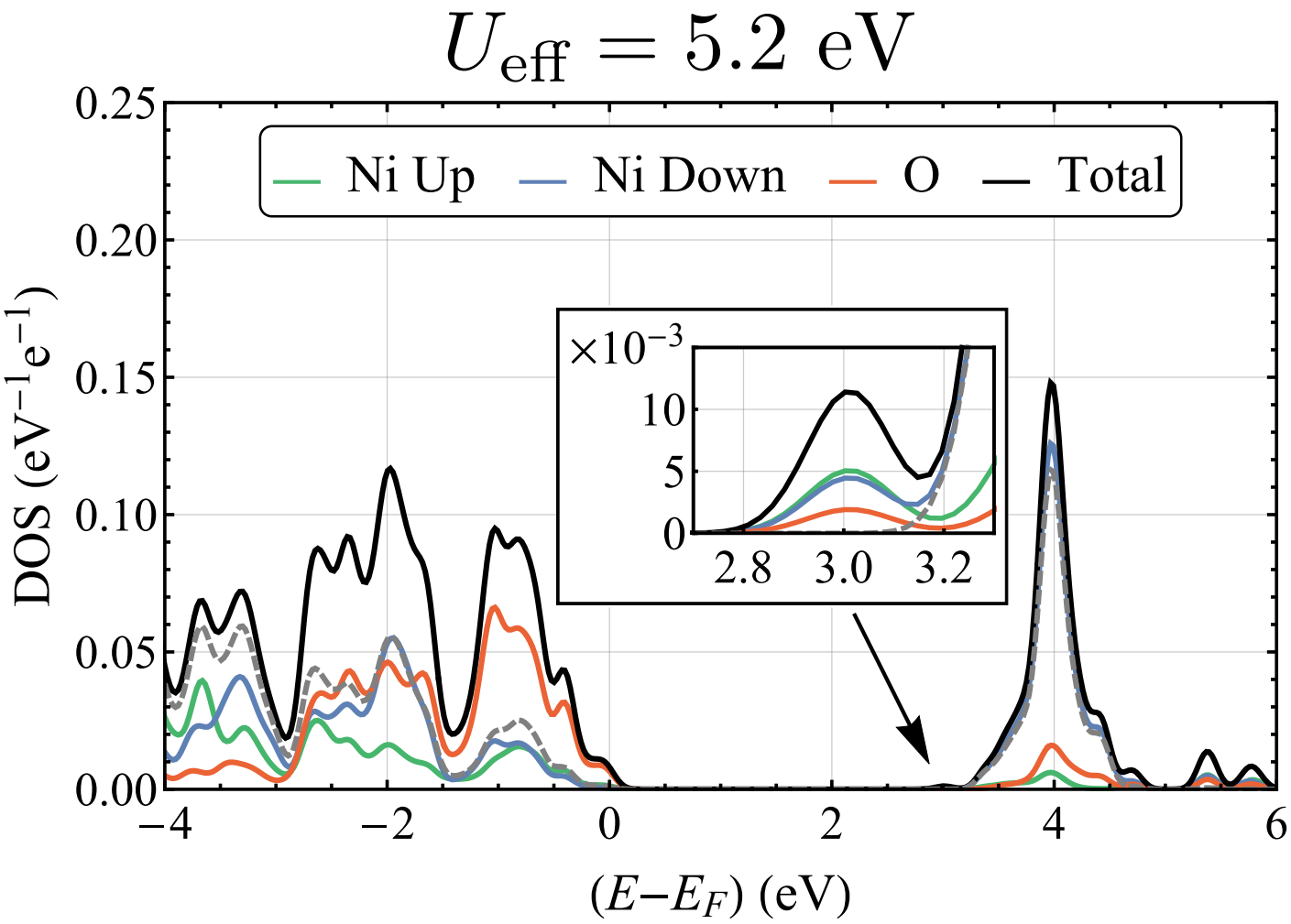
How to quantify SCE on sub-spaces?

- Define J as minus the subspace-averaged rate of change of Hxc potential on magnetism M, w.r.t. M.
- If $$M = \mathrm{Tr}\left[\left(\rho^{\uparrow} - \rho^{\downarrow}\right)\hat{\mathrm{P}}\right]$$
$$v^{M} = \mathrm{Tr}\left[\left(\mathrm{v}^{\uparrow} - \mathrm{v}^{\downarrow}\right)\hat{\mathrm{P}}\right] / 2\mathrm{Tr}\left[\hat{\mathrm{P}}\right]$$
- then $$-J \equiv \frac{dv^{M}_{\mathrm{Hxc}}}{dM} = \chi^{-1}_{M0} - \chi^{-1}_{M}$$
- where $$\chi^{-1}_{M0} = \frac{dv^{M}_{\mathrm{KS}}}{dM}, \quad \chi^{-1}_{M} = \frac{dv^{M}_{\mathrm{ext}}}{dM} = \frac{d\beta}{dM}$$

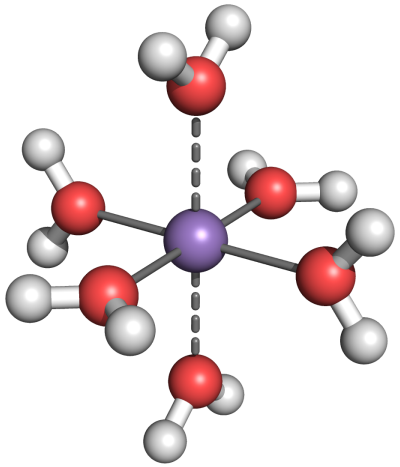
NiO self-consistent DFT(PBE)+(U-J) DoS

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

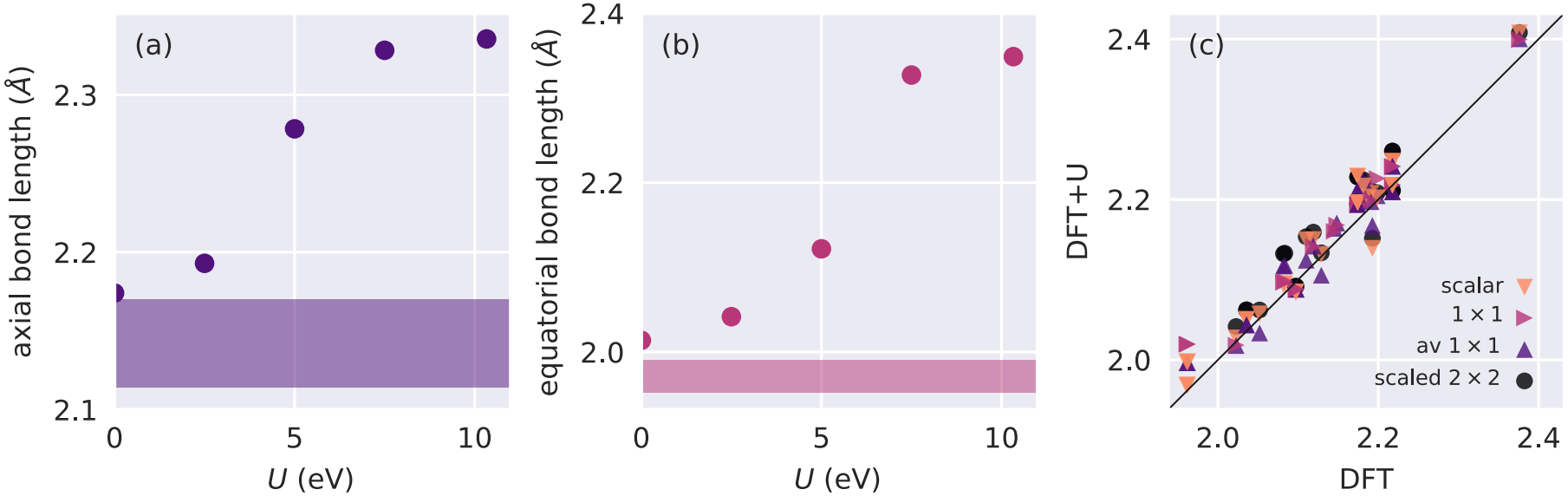
PBE+U: Band gap = 3.0 eV Mag. Mom. = 1.57 μB



Effect of O 2p correction terms on geometries

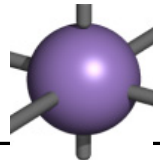


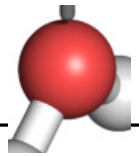
- For details on Hund's J calculation, see:
  E. B. Linscott, D. J. Cole, M. C. Payne, and
  D. D. O'Regan, Phys. Rev. B **98**, 235157 (2018).
- For ionic forces and nonorthogonal population analysis schemes in DFT+U and related methods:
  D. D. O'Regan, M. C. Payne, and A. A. Mostofi
  Phys. Rev. B **83**, 245124 (2011).



Are only TM 3d orbitals error-prone?

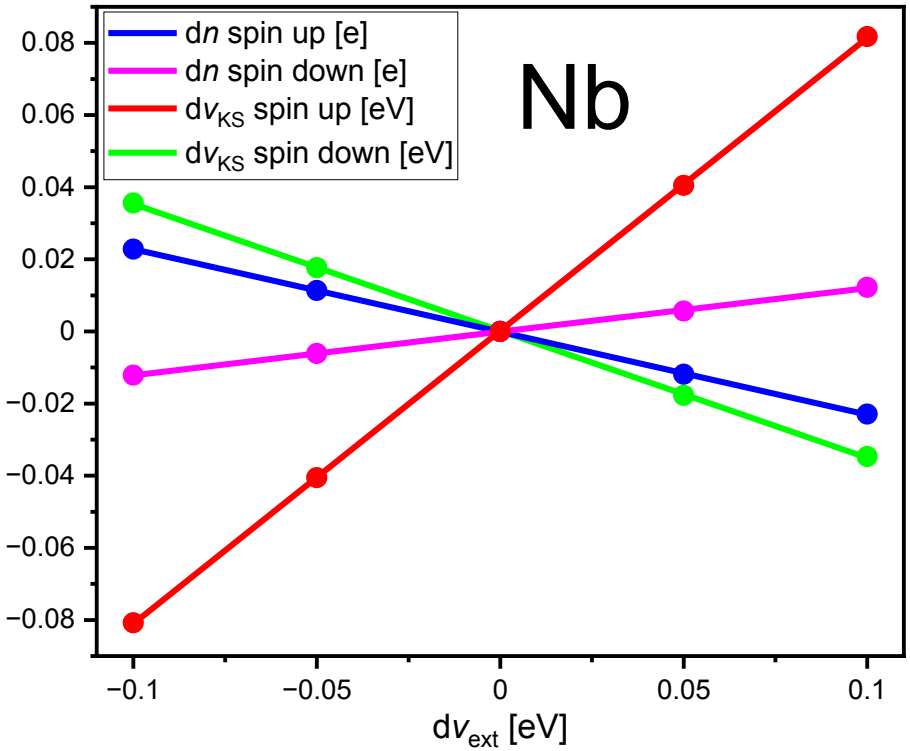
- Oxygen 2p orbitals often harbour large U values.

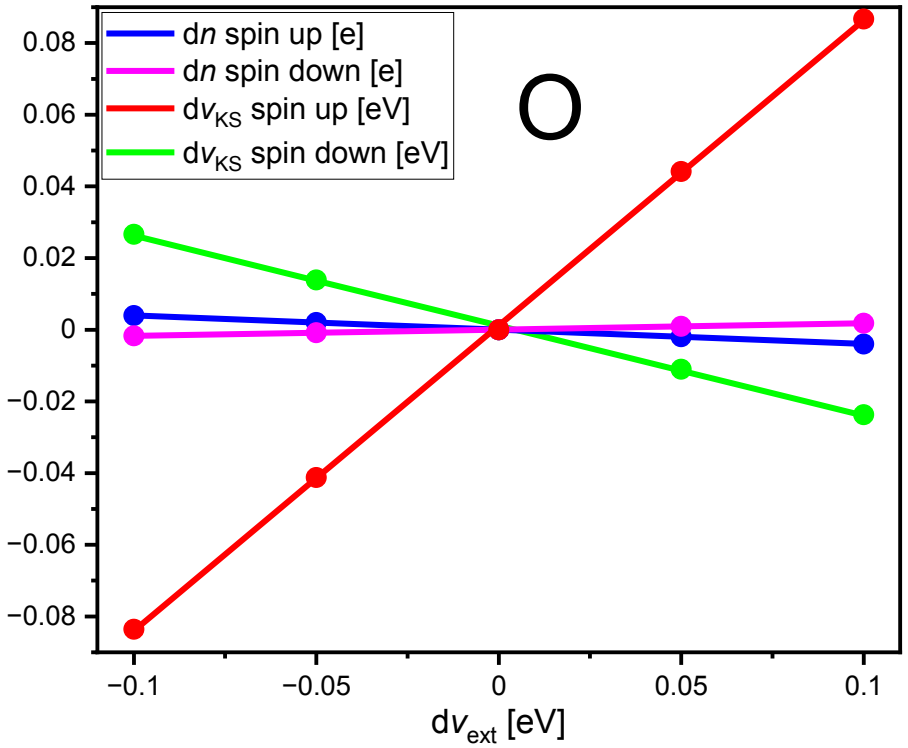


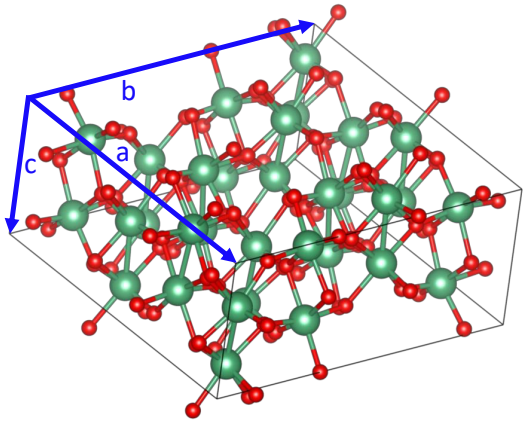


Metal	U	J	U	J
Ti^{3+}	3.89 ± 0.01	0.34 ± 0.00	8.13 ± 0.02	1.05 ± 0.00
V^{2+}	4.00 ± 0.01	0.35 ± 0.00	8.28 ± 0.01	1.29 ± 0.00
Cr^{3+}	3.90 ± 0.01	0.42 ± 0.00	8.29 ± 0.02	1.08 ± 0.01
Cr^{2+}	3.20 ± 0.01	0.35 ± 0.00	8.45 ± 0.02	1.27 ± 0.01
Mn^{3+}	5.40 ± 0.01	0.53 ± 0.00	8.57 ± 0.03	0.97 ± 0.01
Mn^{2+}	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

Computing U and J in ONETEP (example: NbO_2)







	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

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

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

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

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

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

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

- 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 TiO_2

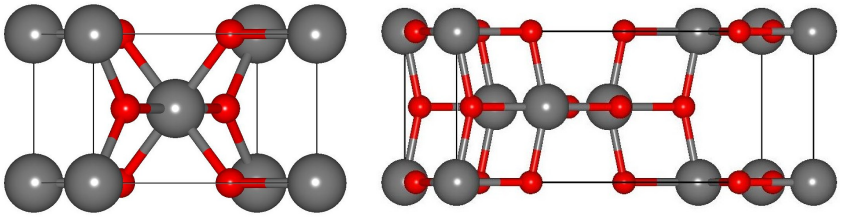
TiO_2-rutile E_{gap}		
DFT (LDA)	1.96	
	U^d	$U^{d,p}$
DFT+U	2.24	3.59
DFT+$U_{eff} = U - J$	2.21	3.38
DFT+$U_{full} = U - 2J, \alpha = -J/2$	2.17	3.32
DFT+$U_{full} = U - 2J$	2.18	3.18
DFT+$U_{full} = U - 2J, \alpha = J/2$	2.20	**3.04**
DFT+U+J (no minority spin term)	2.20	**3.04**
Experiment [12, 13]		**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_0W_0 [18]	3.34
PBE+G_0W_0 [19]	3.46
HSE+G_0W_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 TiO_2

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_0W_0 [18]		3.56
PBE+G_0W_0 [11]		3.61
PBE+G_0W_0 [19]		3.73
HSE+G_0W_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

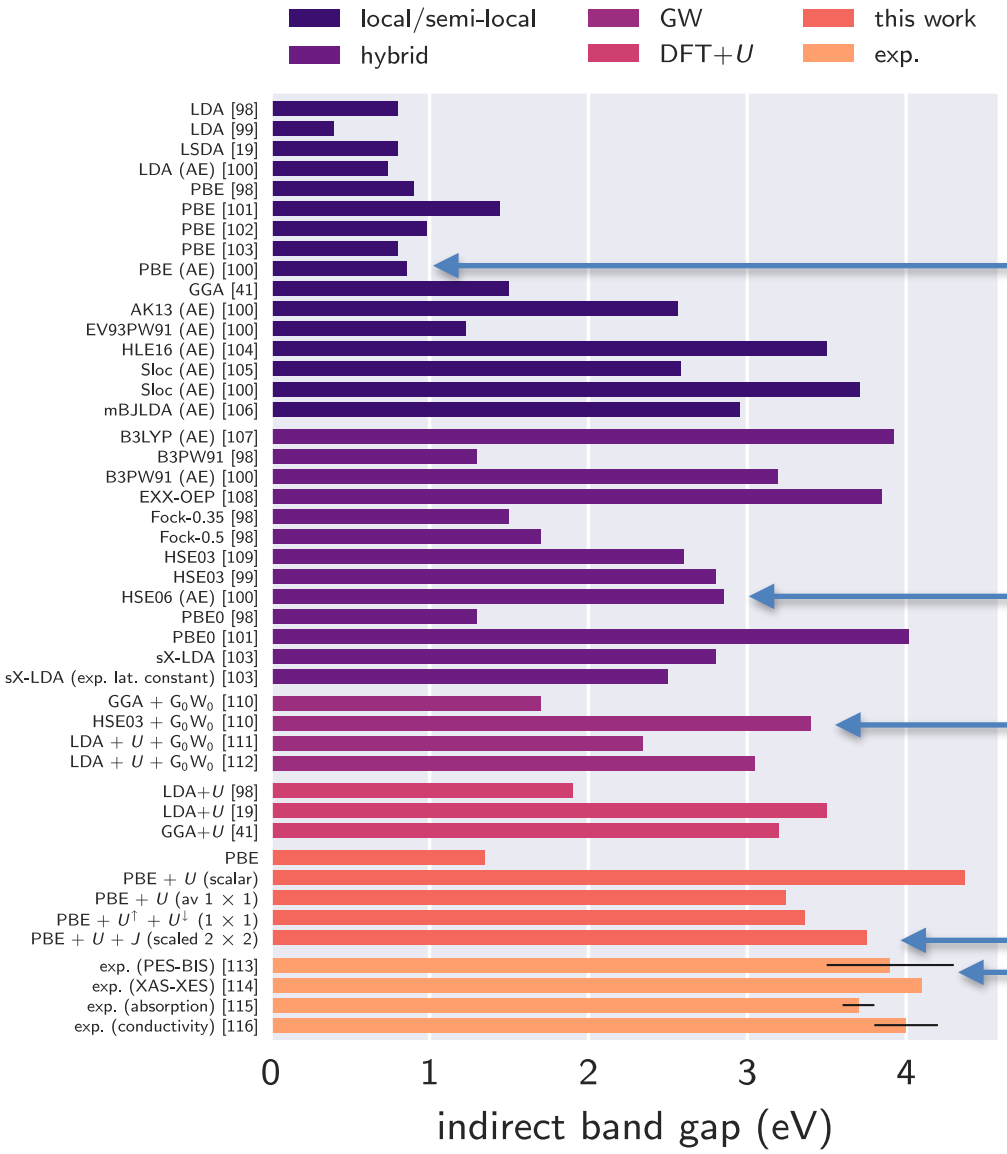


(a) Rutile (b) Anatase

TiO_2-rutile E_{gap}				
Subspace definition	Ti^0		Ti^{3+}	
DFT(LDA)	1.96		1.96	
	$+U^d$	$+U^{d,p}$	$+U^d$	$+U^{d,p}$
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: another challenging test for DFT



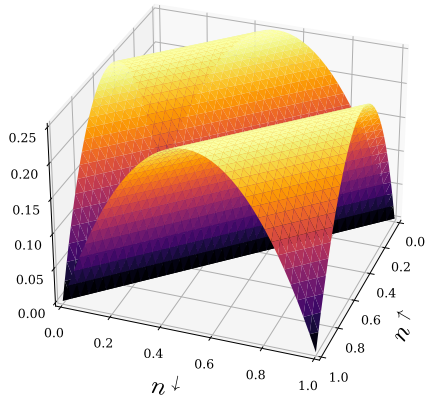
- Standard DFT
- HSE hybrid DFT
- Many-body beyond DFT
- DFT+U+J (cost similar to DFT)
- Best available experiment

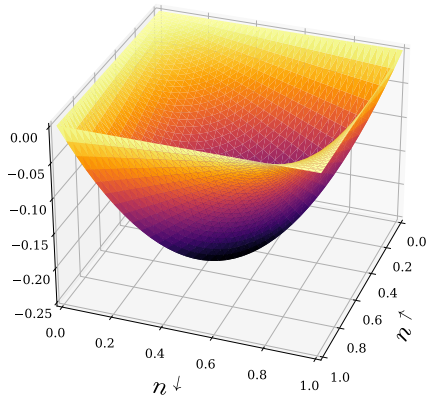
ONETEP as an aid to functional development

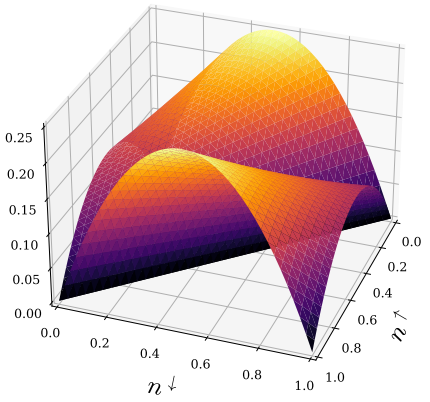
- BLOR is an exactified DFT+U functional based on idea of measuring and correcting self-interaction and static correlation error in situ. For single-orbital subspaces, it can be shown to be unique, and it differs from conventional DFT+U+J.

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

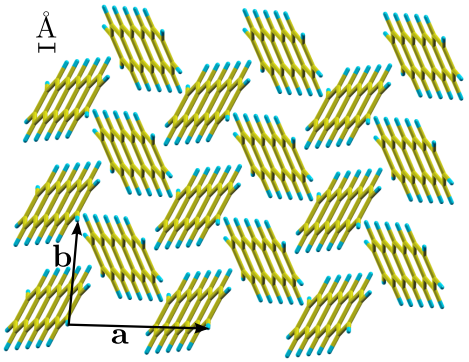
$$\hat{P} = \sum_m |\phi_m\rangle \langle \phi^m| \qquad \hat{n}^{\sigma} = \hat{P}\hat{\rho}^{\sigma}\hat{P} \qquad \hat{N} = \hat{n}^{\uparrow} + \hat{n}^{\downarrow} \qquad \hat{M} = \hat{n}^{\uparrow} - \hat{n}^{\downarrow}$$

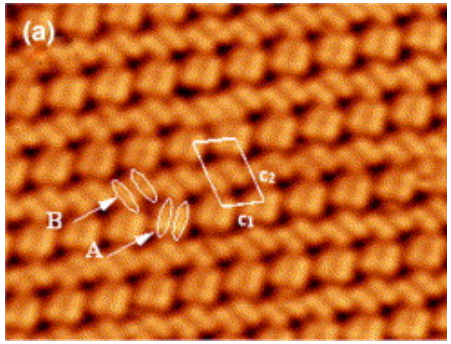




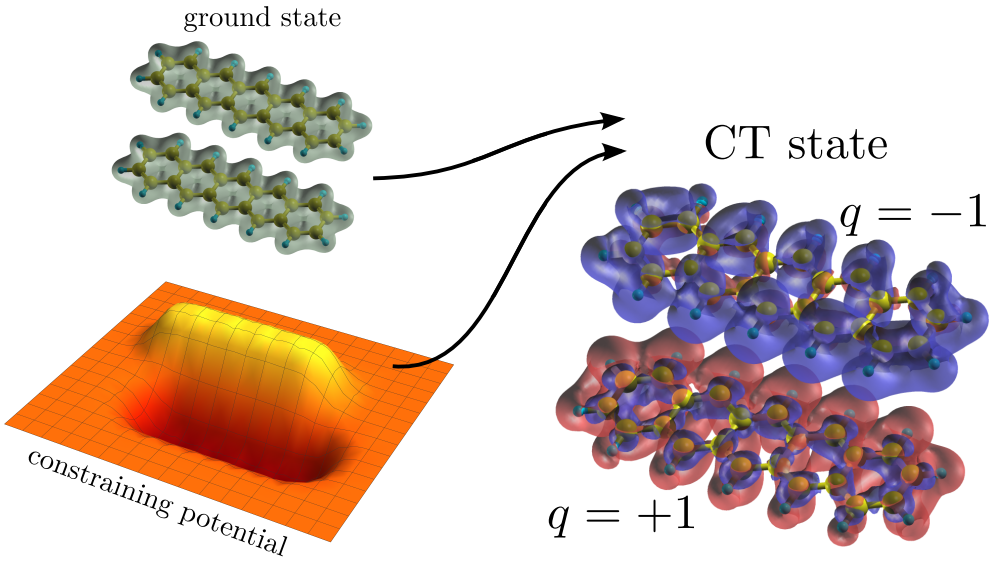


Illustrating cDFT: charge-transfer in pentacene



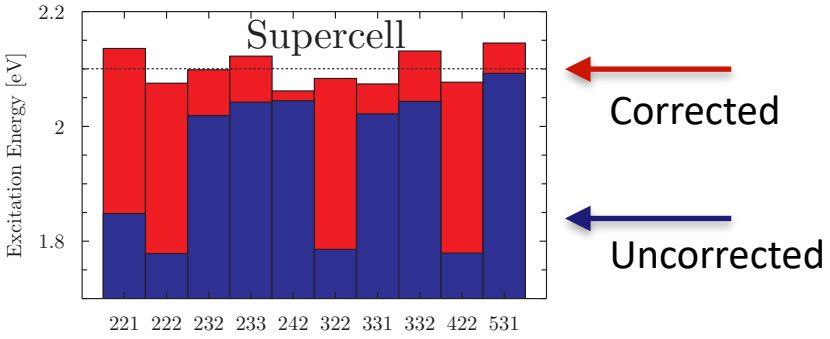


– J.-Z. Wang, et al, Surface Science **579**, 80 (2005).



– Orbital-based constrained DFT allows to measure DFT errors, selectively excite systems, and investigate transient states.

Configuration	our method	CASPT2/CASSCF	GW/BSE
Herringbone 1	2.04	2.22 [47]	1.92 [47]
Herringbone 2	2.72	2.55 [47]	2.60 [47]
Parallel	2.61	3.03 [47]	2.45* [47]

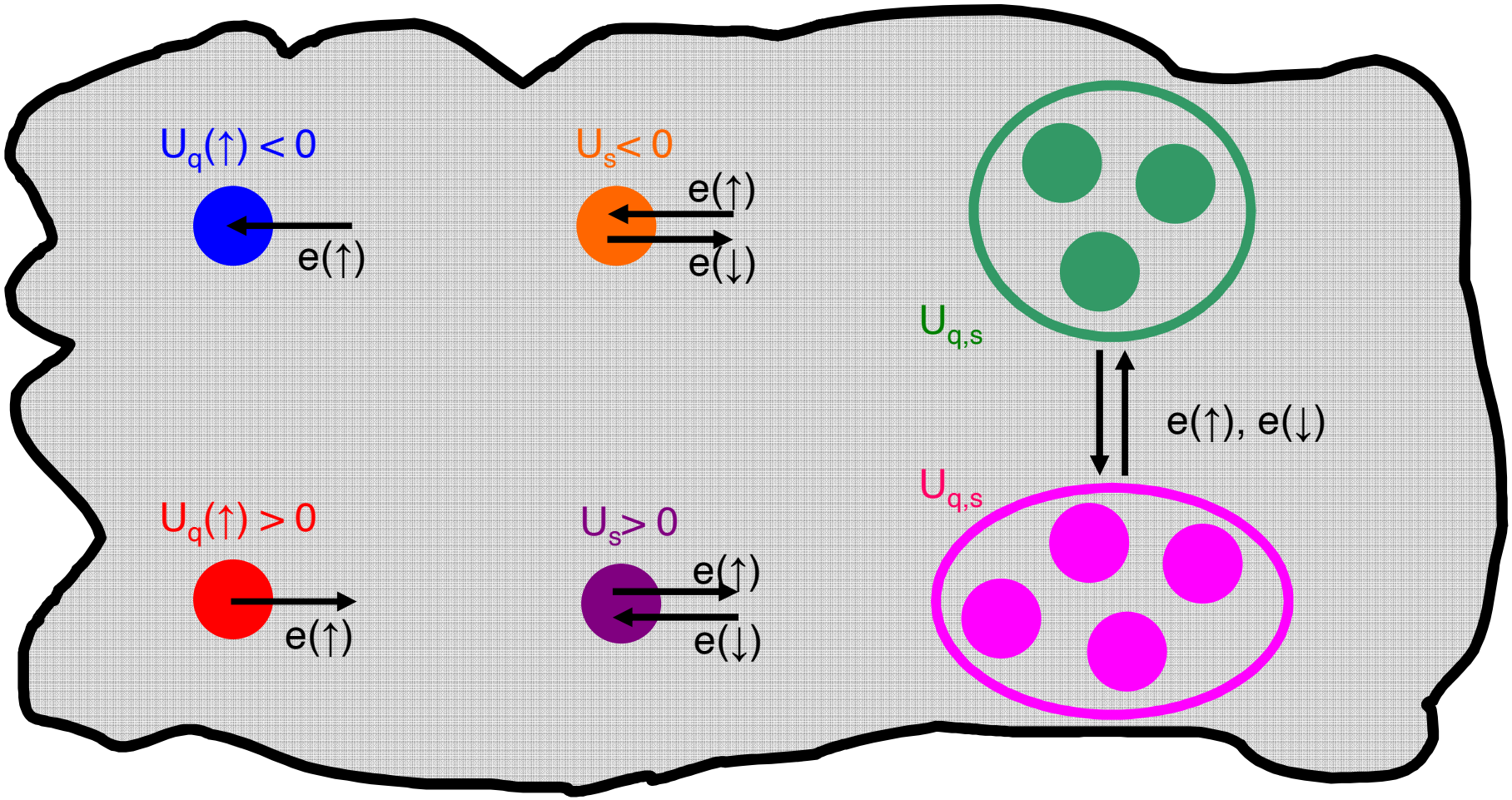


– Variational cDFT optimizability proof: D. D. O'Regan and G. Teobaldi, Phys. Rev. B **94**, 035159 (2016).

– Periodic boundary correction shown here: D. Turban, et al., Phys. Rev. B **93**, 165102 (2016).

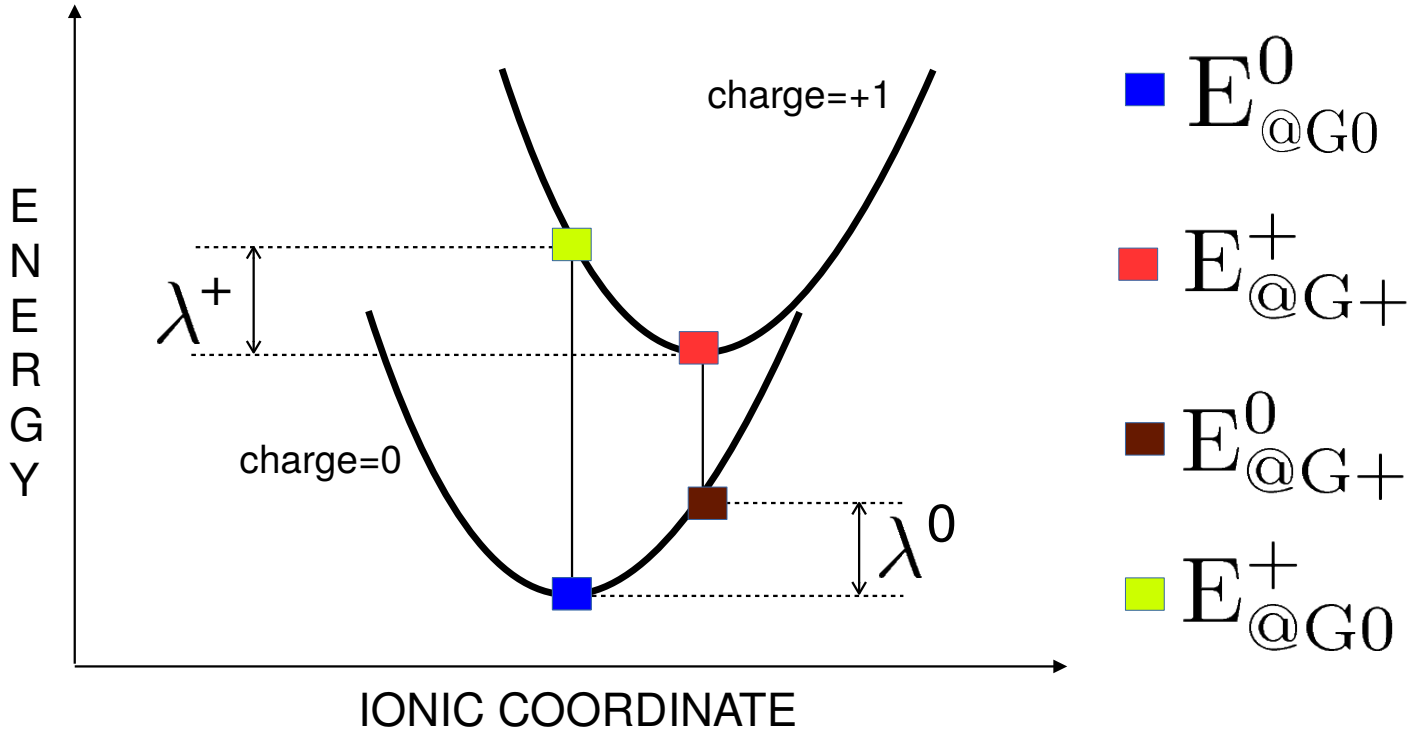
So, what are we doing in practice?

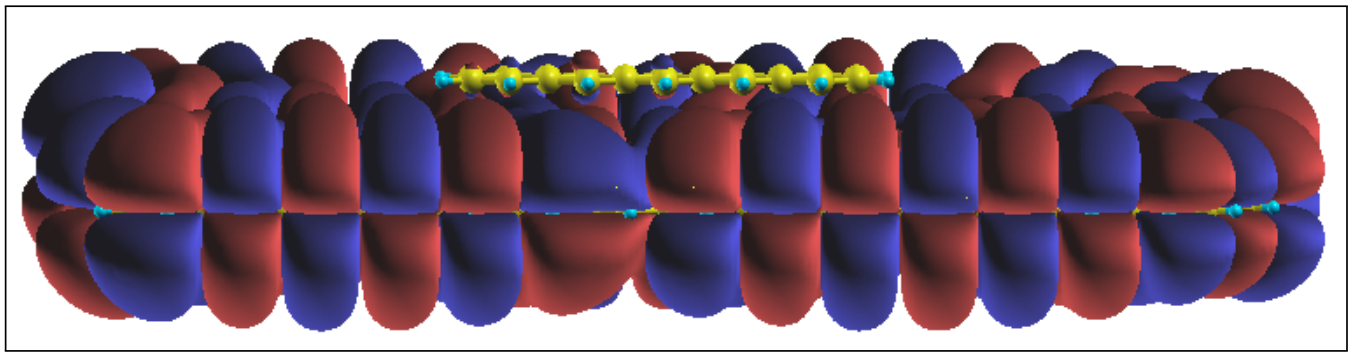
…(just) adding attractive/repulsive potentials to **constrain** subspace **populations**, **population differences**, and/or **magnetic moments** (**differences**)



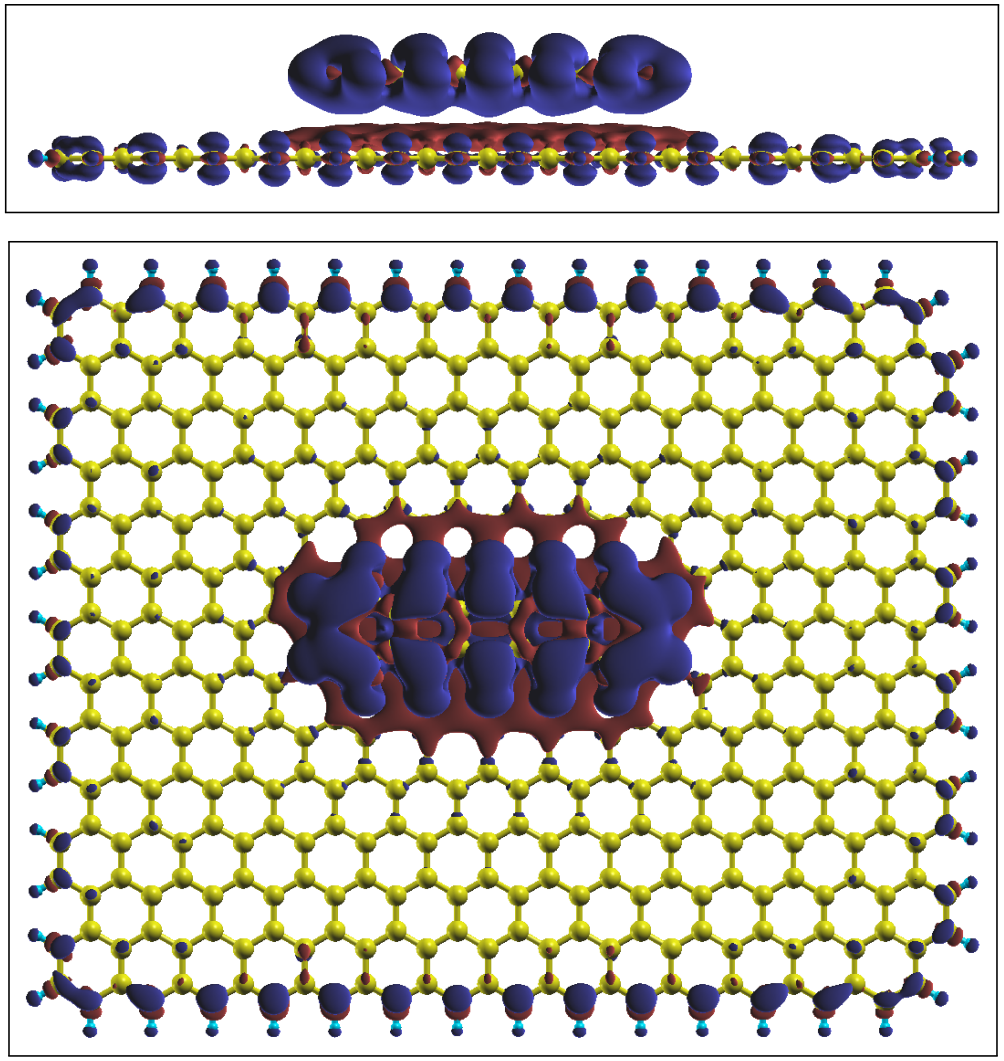
$$E_{cDFT} = E_{DFT} + \sum_{I=1}^{N_{sites}} \sum_{\sigma=1}^{2} U_q^{(I)(\sigma)} \left(Tr\left[n^{(I)(\sigma)}\right] - N_{(I)(\sigma)} \right) + \sum_{I=1}^{N_{sites}} U_s^{(I)} \left(Tr\left[n^{(I)(\uparrow)}\right] - Tr\left[n^{(I)(\downarrow)}\right] - \Delta N_{(I)} \right)$$

A challenge for cDFT: the reorganization effect



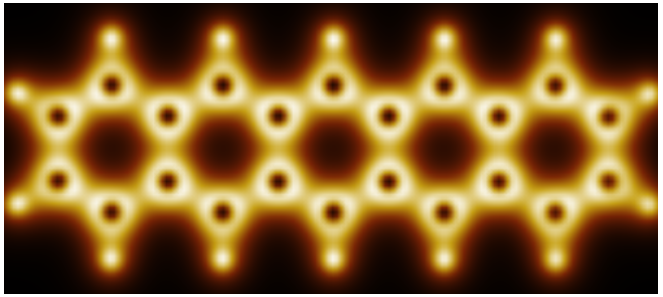


How to define the constrained population?



Summed atomic population **172.72**

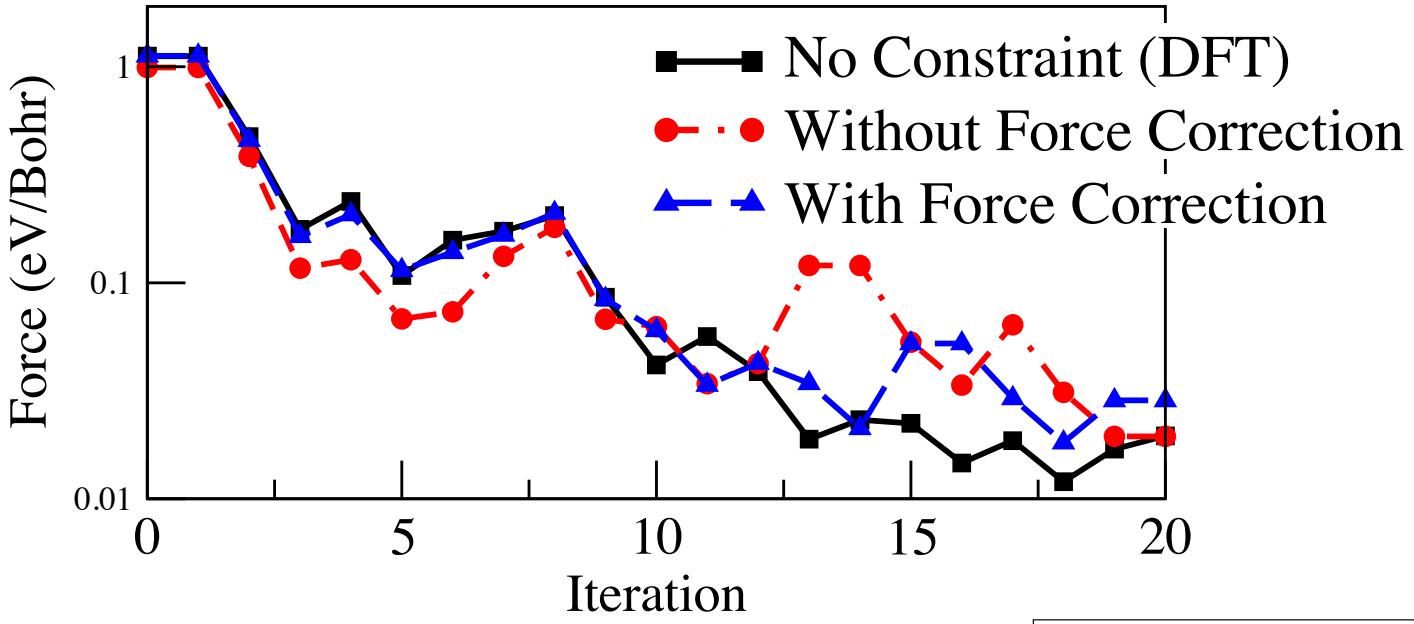
Expected Population **102**

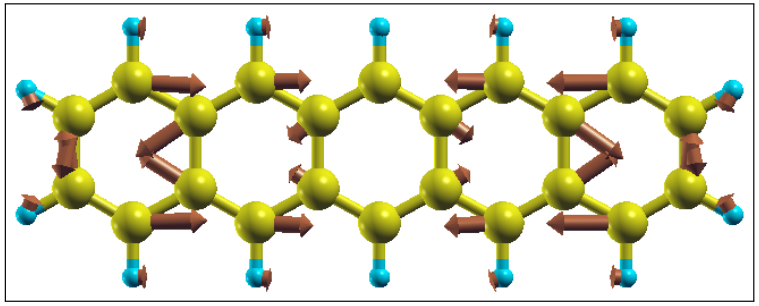


$$\langle r | \hat{\mathbb{P}} | r \rangle$$

- S. Roychoudhury, D. D. O'Regan, and S. Sanvito, Phys. Rev. B **97**, 205120 (2018).

Pulay force due to variable nonorthogonality

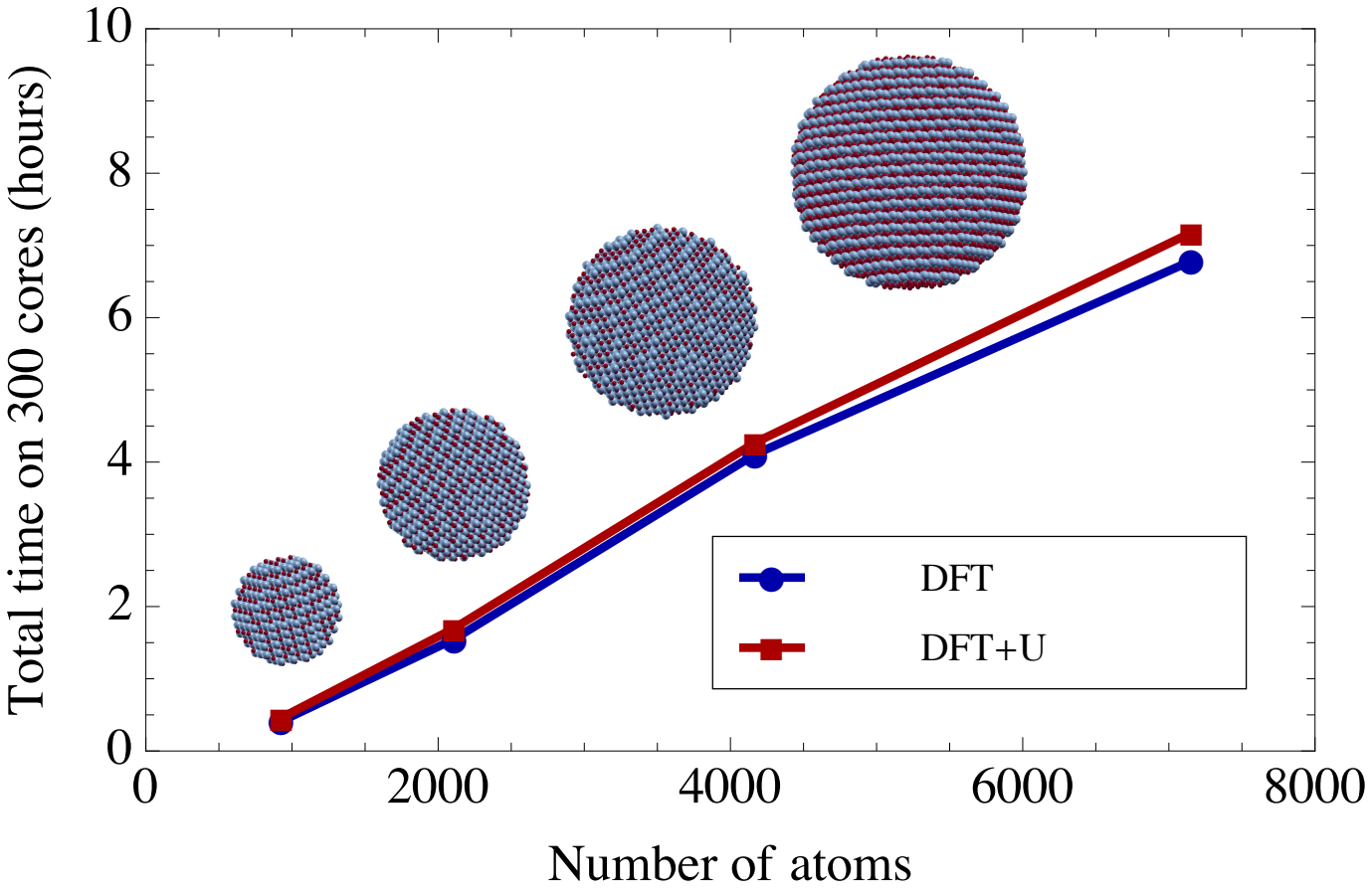




- Reorganization energy (meV)

Cutoff energy	flake	λ^0	λ^+	λ	ΔV_c
900 eV	none	29	27	56	N.A.
900 eV	smaller	23	26	49	44
900 eV	larger	20	20	39	50
1500 eV	none	29	27	56	N.A.
1500 eV	smaller	25	25	51	45
1500 eV	larger	17	23	40	33

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).

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Coláiste na Tríonóide, Baile Átha Cliath
The University of Dublin

Thank you for listening

Chat here or contact for any DFT+U, cDFT, or oxide physics support at:

- David.O.Regan@tcd.ie
- @OReganGroupTCD
- www.theoryofmaterials.com

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