

The motivation, theory, and application of DFT+ U

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04/22/14

Outline

- The source of the self-interaction error in DFT
- The effects of the self-interaction error in DFT
- A proposed solution – the Hubbard U
- Empirical usage of the Hubbard U
- Calculation of the Hubbard U

Difficulty of solving the Schrodinger Equation

$$\left\{ -\frac{\hbar^2}{2m} \sum_j \nabla_j^2 - \sum_{j,l} \frac{Z_l e^2}{|\mathbf{r}_j - \mathbf{R}_l|} + \frac{1}{2} \sum_{j \neq j'} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_{j'}|} \right\} \Psi = E \Psi$$

where $\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$

- For a system with n electrons, we have $3n$ variables ($6n$ including spin)
- A computational and numerical nightmare and infeasible for systems with greater than around 10 electrons

Kohn-Sham Equations used in DFT

$$\left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \sum_l \frac{Z_l}{|\mathbf{r}_j - \mathbf{R}_l|} + \int \frac{n(\mathbf{r}')}{|\mathbf{r}_j - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(n(\mathbf{r})) \right\} \phi_j = \epsilon_j \phi_j$$
$$n(\mathbf{r}) = \sum_{j=1}^N |\phi_j|^2$$

- DFT allows one to reformulate the Schrodinger equation to be in terms of the electron density in stead of the electronic wavefunction
- Now the equation can be solved in terms of the electron density at each point in space \rightarrow 3 parameters (or 6 for spin systems)

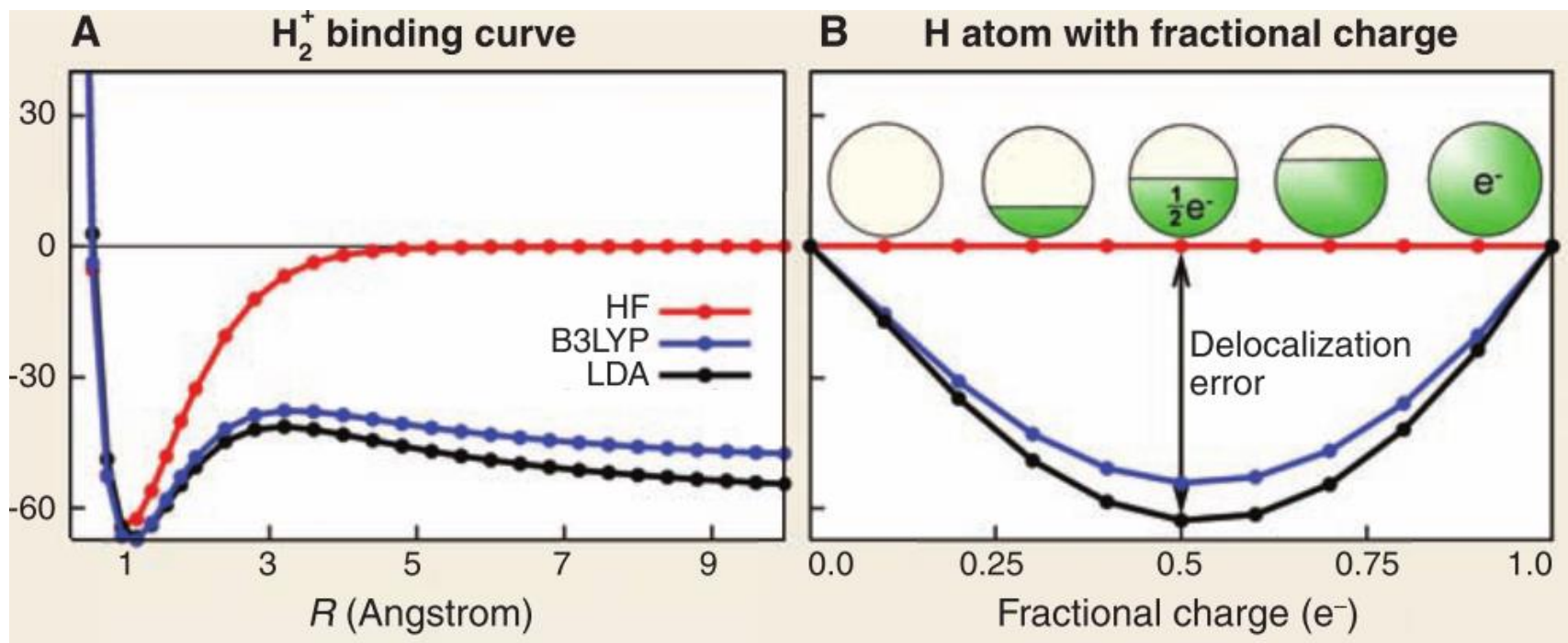
The source of the self-interaction error

$$\left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \sum_l \frac{Z_l}{|\mathbf{r}_j - \mathbf{R}_l|} + \int \frac{n(\mathbf{r}')}{|\mathbf{r}_j - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(n(\mathbf{r})) \right\} \phi_j = \epsilon_j \phi_j$$

$$n(\mathbf{r}) = \sum_{j=1}^N |\phi_j|^2$$

- Electron-electron repulsion term, calculated as the repulsive energy that each electron feels against the entire electron density
- However, the entire electron density inevitably contains that electron as well \rightarrow produces self-interaction error
- Exchange correlation functional $V_{xc}(n(\mathbf{r}))$ meant to take care of this, but it can only be done approximately
- A common effect of this error is electron **delocalization**

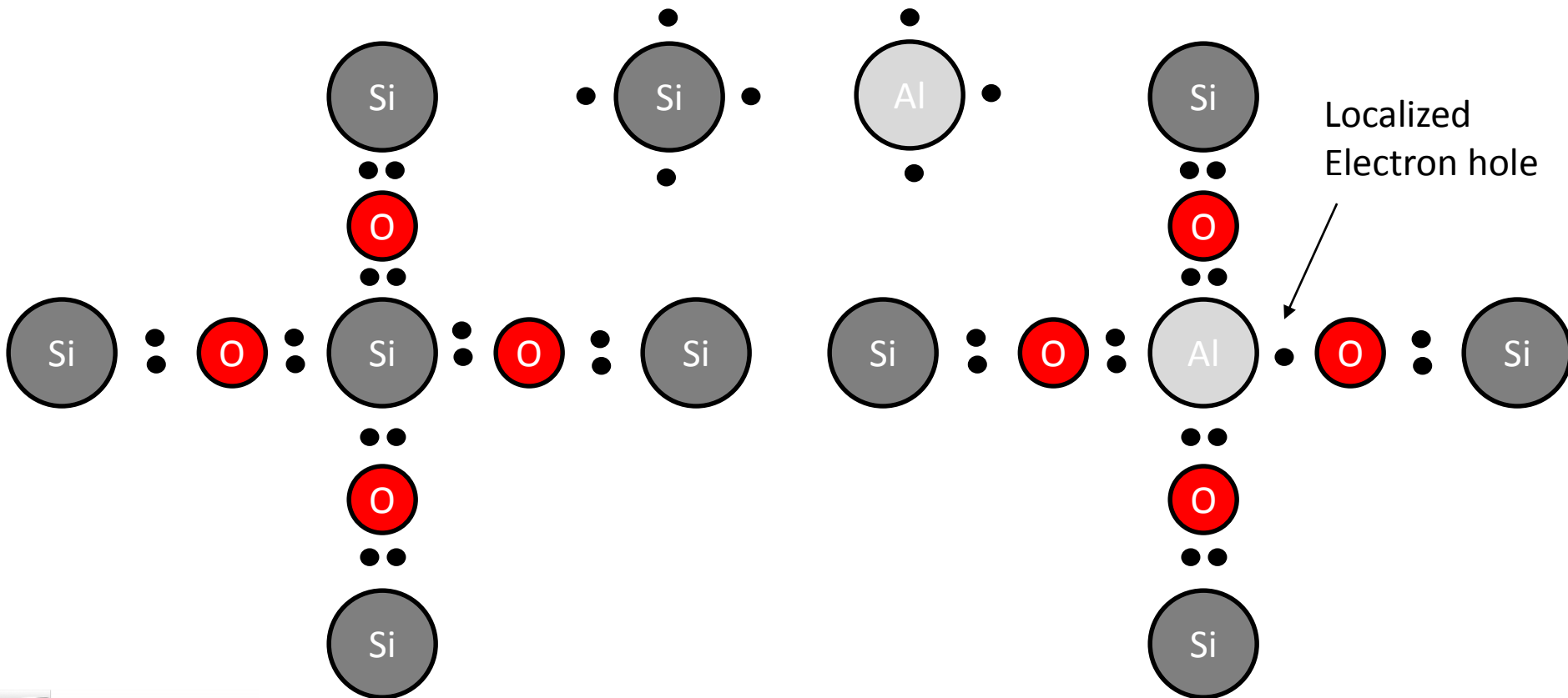
Self-interaction and delocalization error



- Self-interaction error causes electrons to over delocalize into fractional charges that lower the total energy

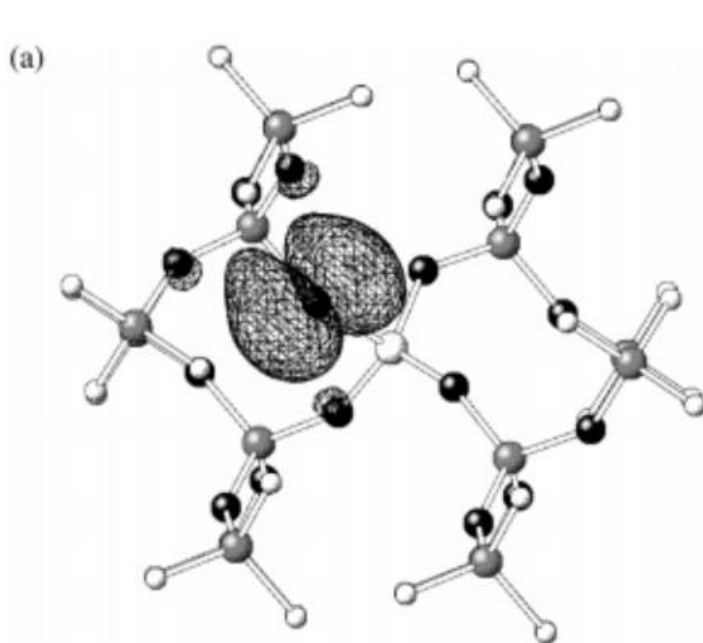
Effects of self-interaction error: electronic structure

- Experimentally, an electron 'hole' in a material should be localized at one site
- A well known example is the creation of a hole by doping Al into SiO_4

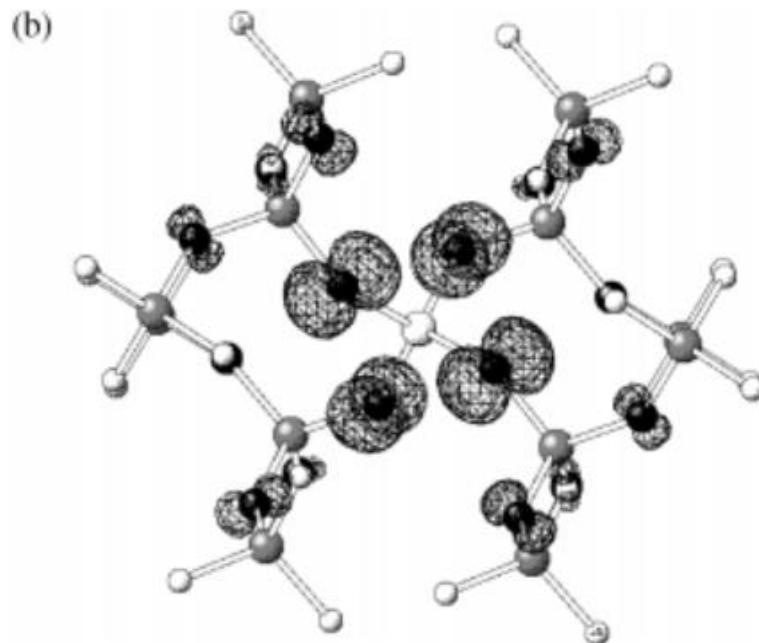


Effects of self-interaction error: electronic structure

- Density functional theory with standard exchange correlation functionals fail to describe the correct localized 'hole' behavior observed by experiments

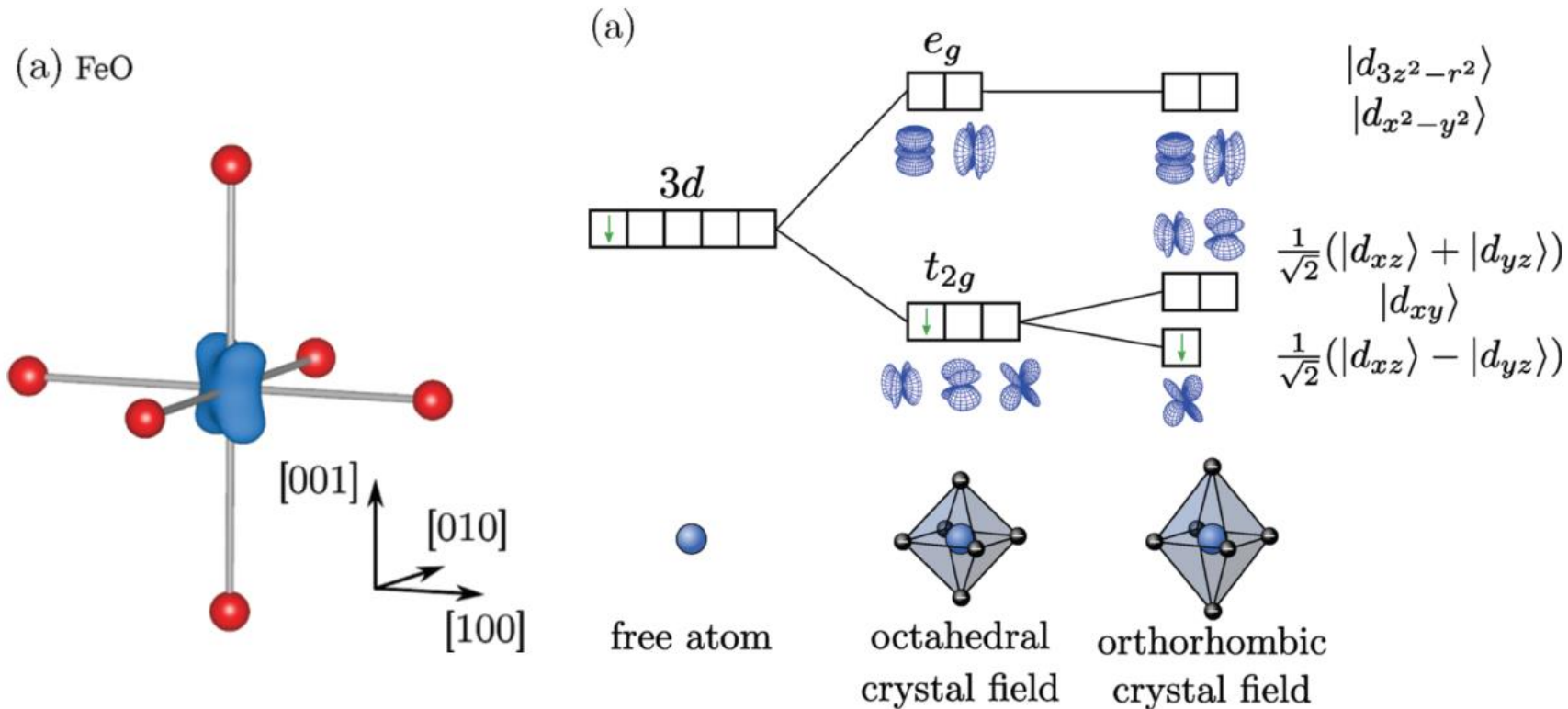


Hartree-Fock
(wavefunction)



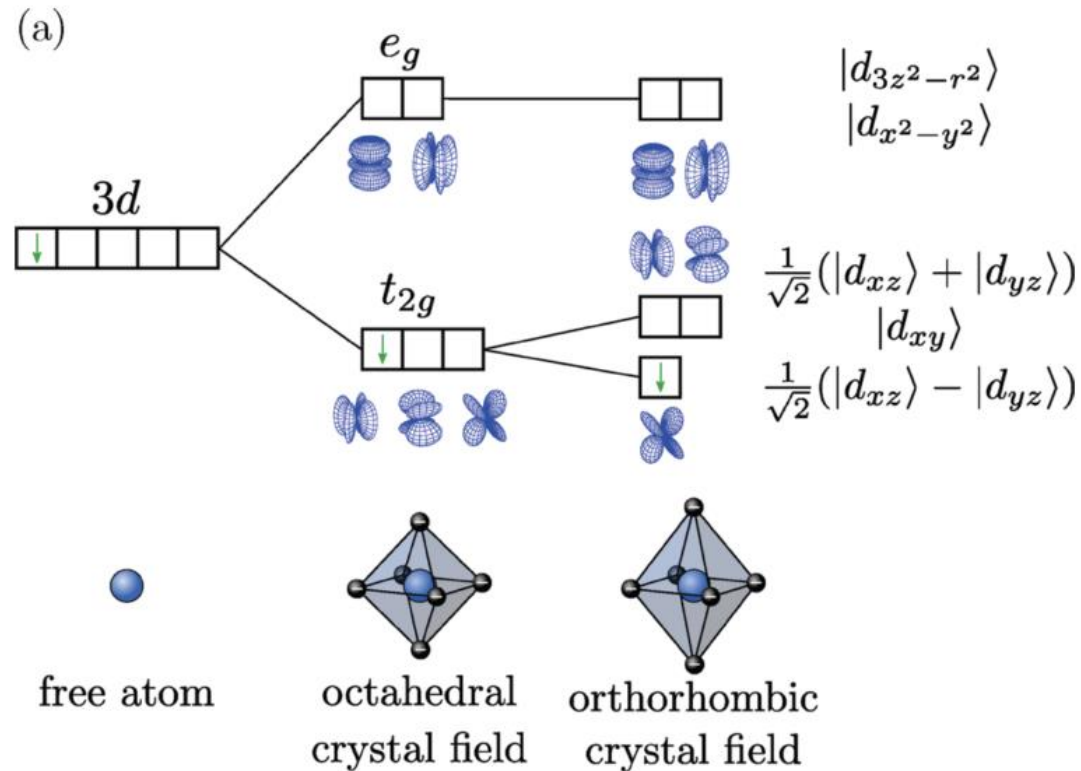
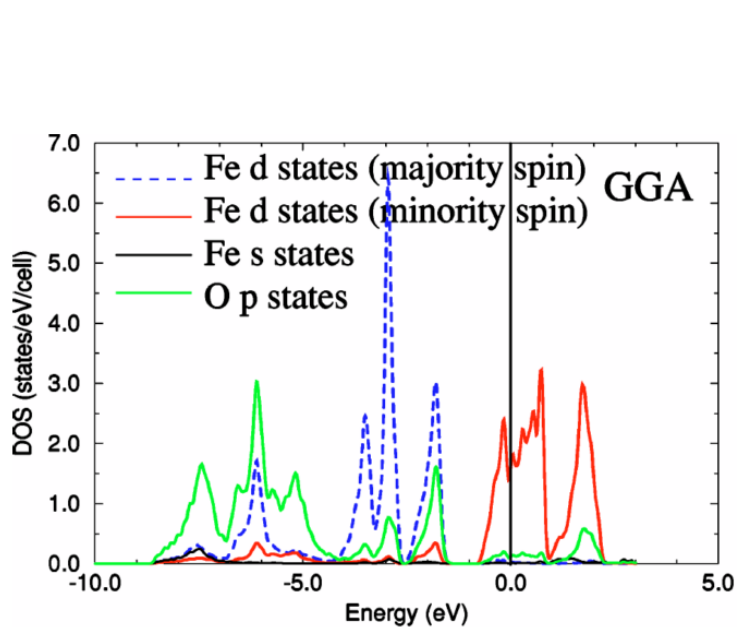
B3LYP
(Density + wavefunction)

Effects of self-interaction error: electronic structure



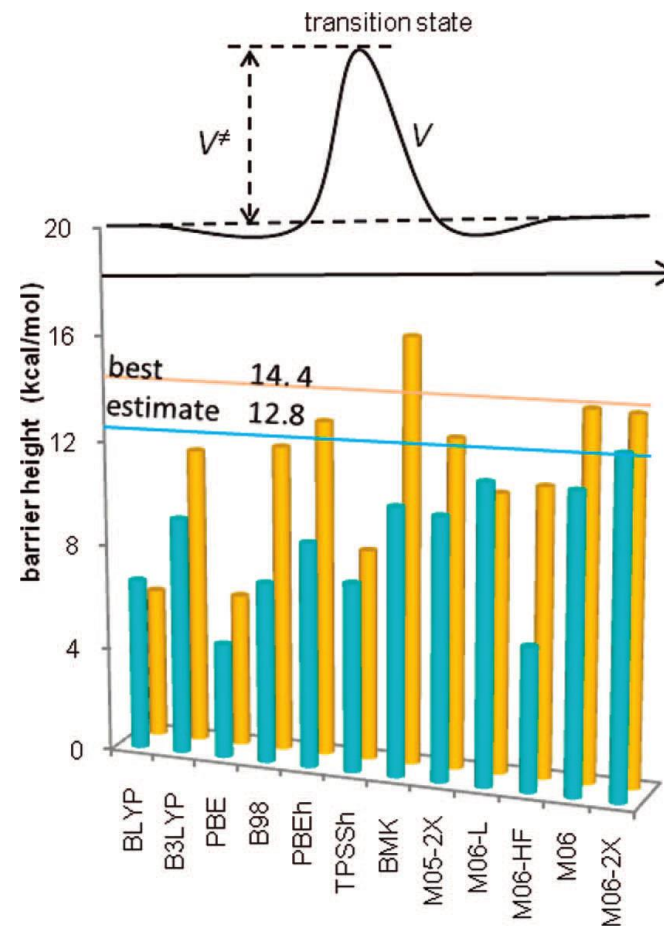
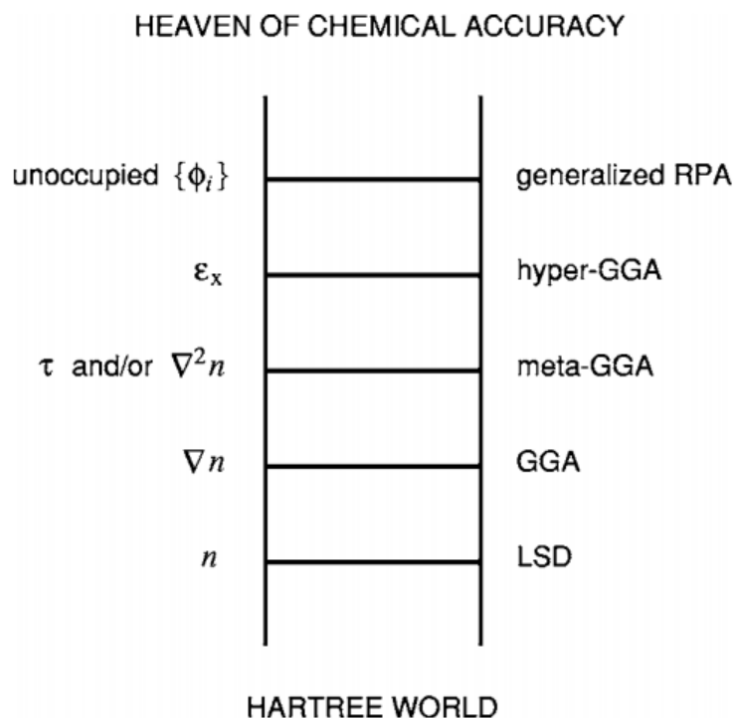
- Rocksalt FeO predicted to have a small bandgap by crystal field theory and observed in experiments

Effects of self-interaction error: electronic structure



- DFT with the GGA exchange correlation functional predicts a metallic state
- Due to over-delocalization of d -electrons caused by self-interaction error

Effects of self-interaction error: kinetics



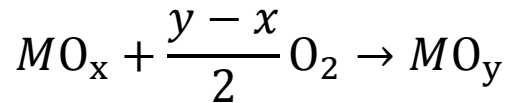
- Obtaining better dissociation barriers means more expensive exchange correlation functionals

■ $\text{HCC} + \text{HCCH} \rightarrow \text{HCCH} + \text{HCC}$

■ $\text{OH}^- + \text{CH}_3\text{OH} \rightarrow \text{HOCH}_3 + \text{OH}^-$

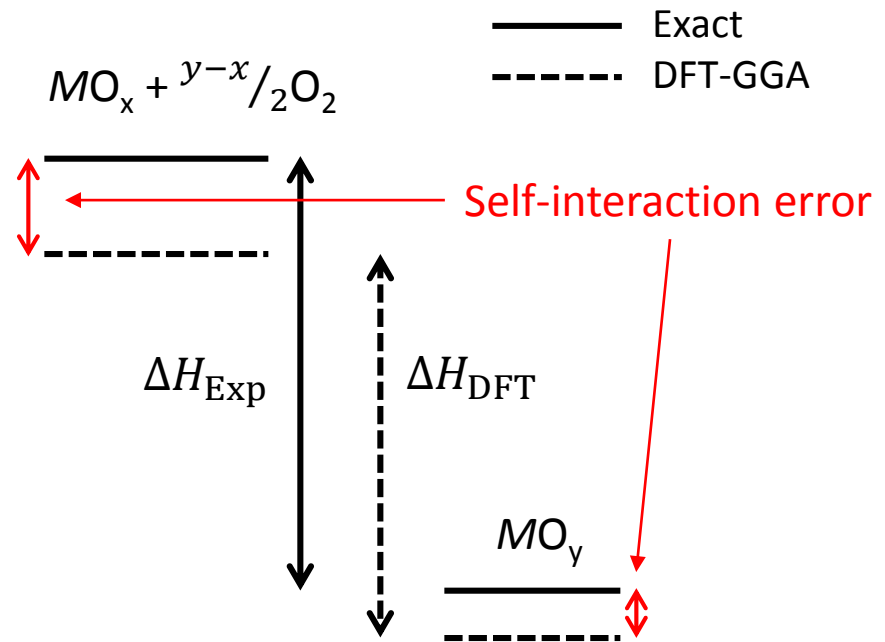


Effects of self-interaction error: thermodynamics

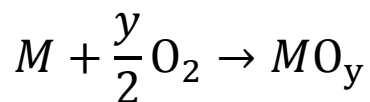


$$\Delta E_{rxn} = E_{MO_y} - \left(E_{MO_x} + \frac{y-x}{2} E_{O_2} \right)$$

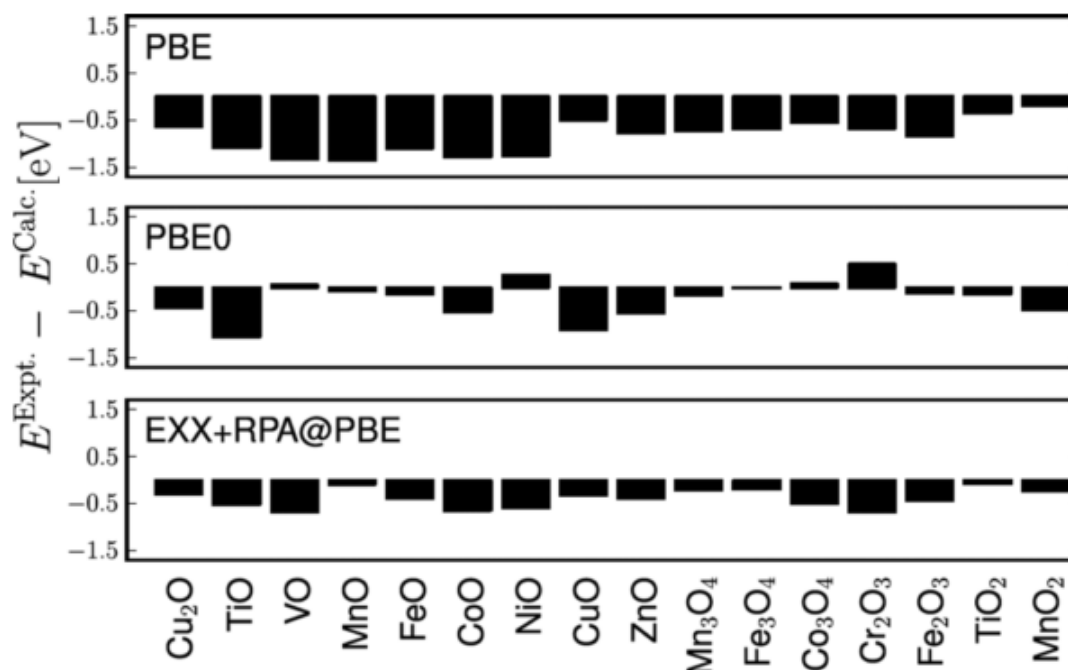
- Differences in self-interaction error produces errors in relative stabilities between materials
- Relative stabilities important for materials discovery



Effects of self-interaction error: thermodynamics



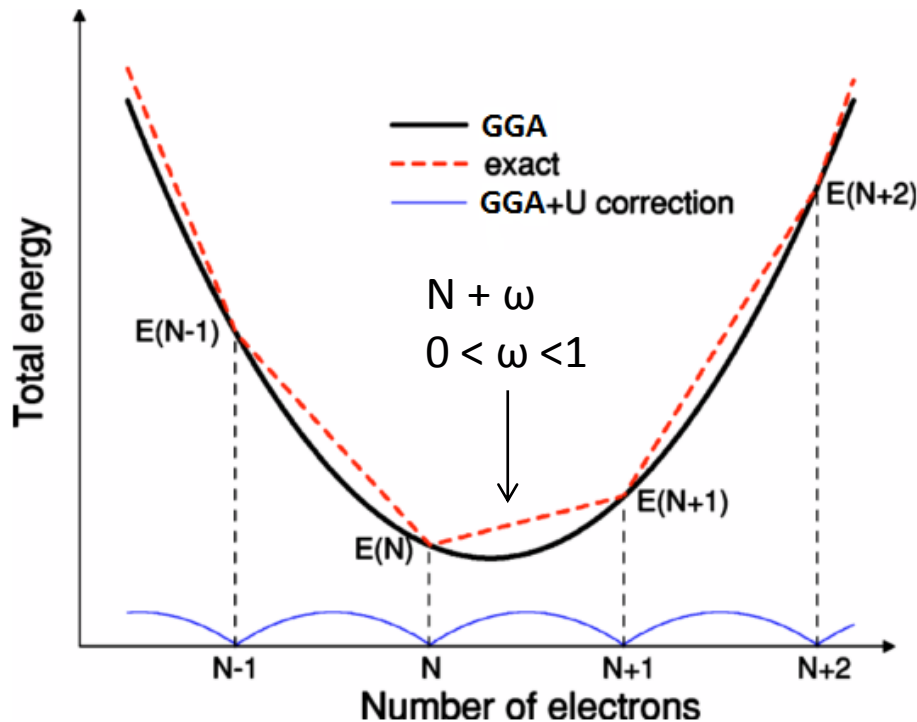
$$\Delta E_{rxn} = E_{\text{MO}_y} - \left(E_M + \frac{y}{2} E_{\text{O}_2} \right)$$



- 3d electrons introduce self-interaction error that are dependent on their electronic environment (metal vs oxide)
- Produces errors in oxidation energies
- Lack of cancellation between self-interaction error in **metals** and **oxides**

The Hubbard U

- The Hubbard U is a penalty applied that depends on the occupancy of the orbital that needs correction for the self-interaction error



$$E_U = \frac{U}{2} \sum_{I,\sigma} \sum_i \lambda_i^{I\sigma} (1 - \lambda_i^{I\sigma})$$

U = Hubbard U λ = occupation
 I = Atom
 σ = Spin

- Penalty matches the error present in DFT GGA and LDA calculations

Applying the Hubbard U in VASP (jasp)

```

#+BEGIN_SRC python
import myproj
from jasp import *
from mybulk import rocksalt
from ase.visualize import view

Us = (0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5)
energies = []
ready = True

bulk = rocksalt(('Mn', 'O'), vol=38.450, mags=(3,0))

for U in Us:
    with jasp('VO/EvsU/U-{:0:1.1f}'.format(U), atoms=bulk,
              xc='PBE', lreal=False,
              encut=520, prec='Accurate',
              kpts=(7, 7, 7), ismear=1, sigma=0.05,
              ibrion=1, isif=6, nsw=50, ediffg=-0.05,
              ispin=2, nupdown=0, lorbit=11,
              ldau=True, ldautype=2, lasph=True, ldauprint=2,
              ldau_luj={'V': {'L':2, 'U':U, 'J':0},
                       'O': {'L':-1, 'U':0, 'J':0}},
              lwave=False) as calc:
        try:
            energies.append(bulk.get_potential_energy())
        except (VaspSubmitted):
            print calc.vaspdir, 'submitted'
        except (VaspQueued, VaspRunning):
            print calc.vaspdir, 'running'

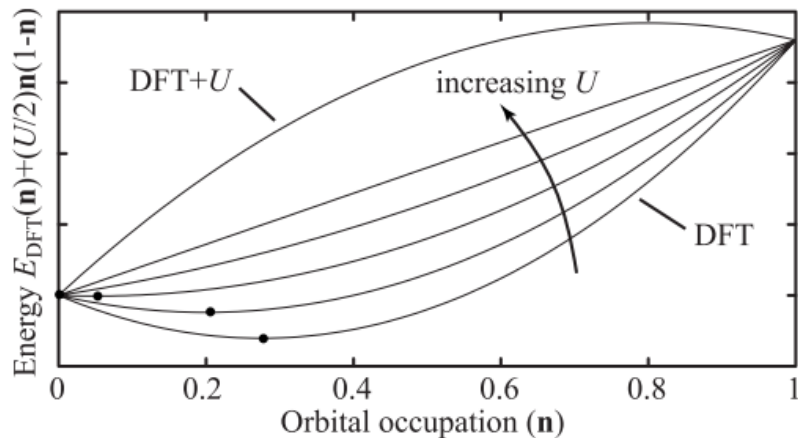
#+END_SRC

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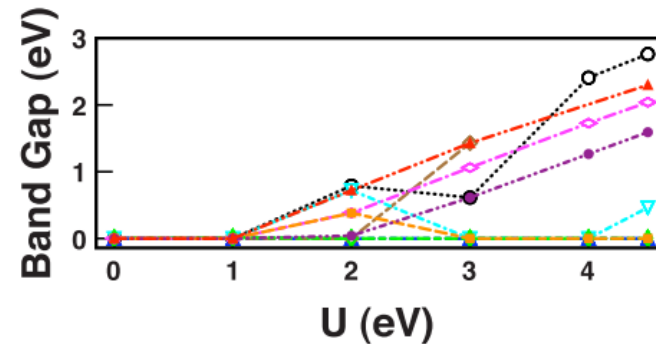
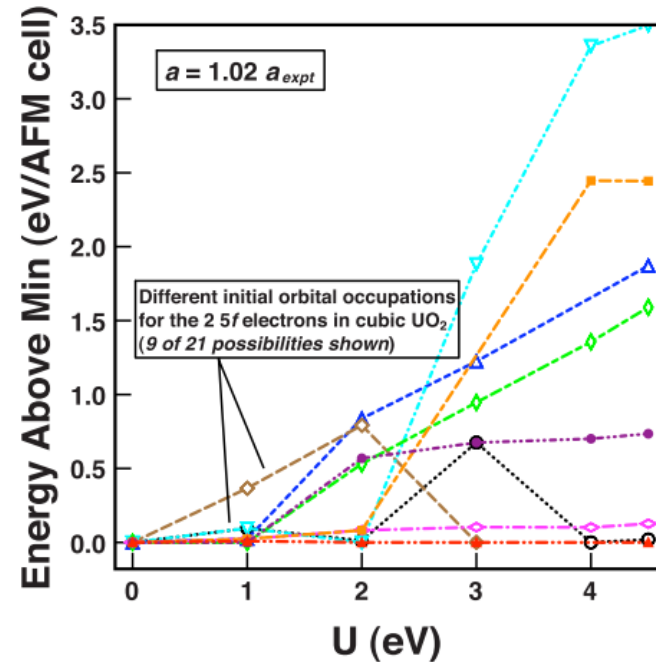
- Very simple, few line application in VASP through jasp
- Little increase in computational time

Usage and interpretation of the results is not as simple → major area of research in all areas of DFT

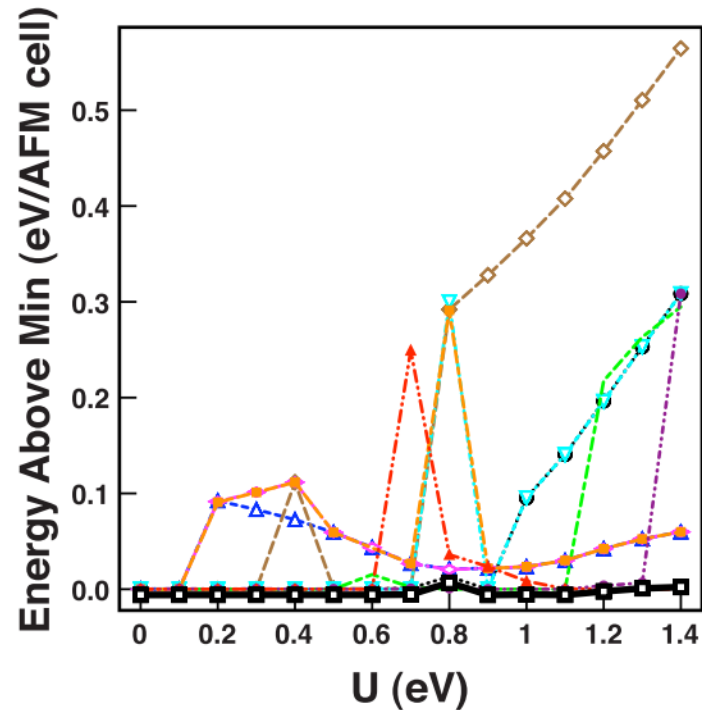
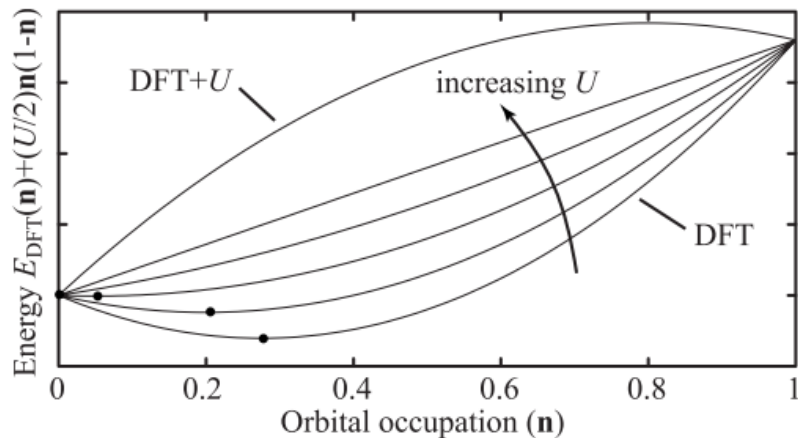
Reaching the ground state with DFT+U



- Application of U might produce multiple local minimal solutions
- Leads to multiple electronically converged structures depending on initialization of the orbitals



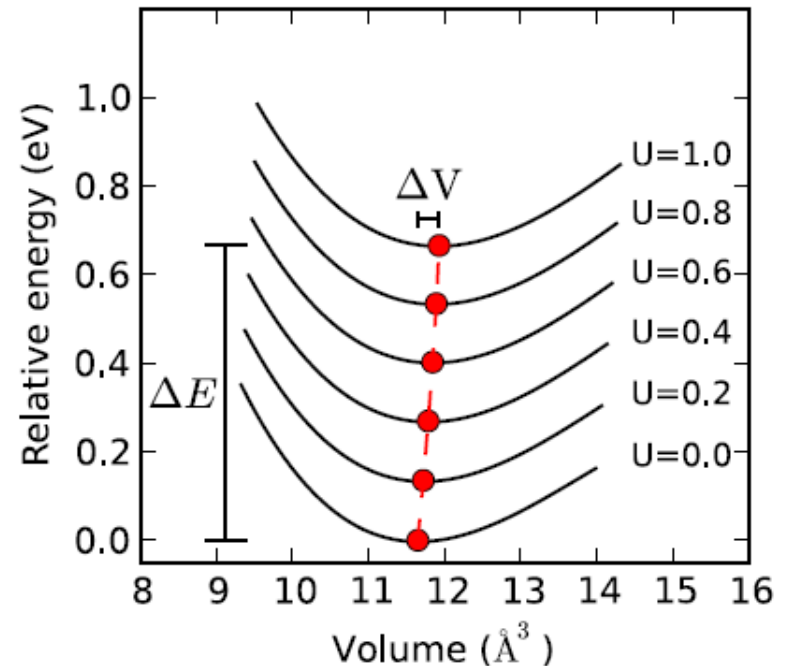
Reaching the ground state with DFT+U



- U ramping solution \rightarrow calculate the electronic structure at slowly increasing U values and using the electronic structure from a previous calculation
- Shown to consistently reach the ground state in energy in many materials (atoms, metals, oxides)

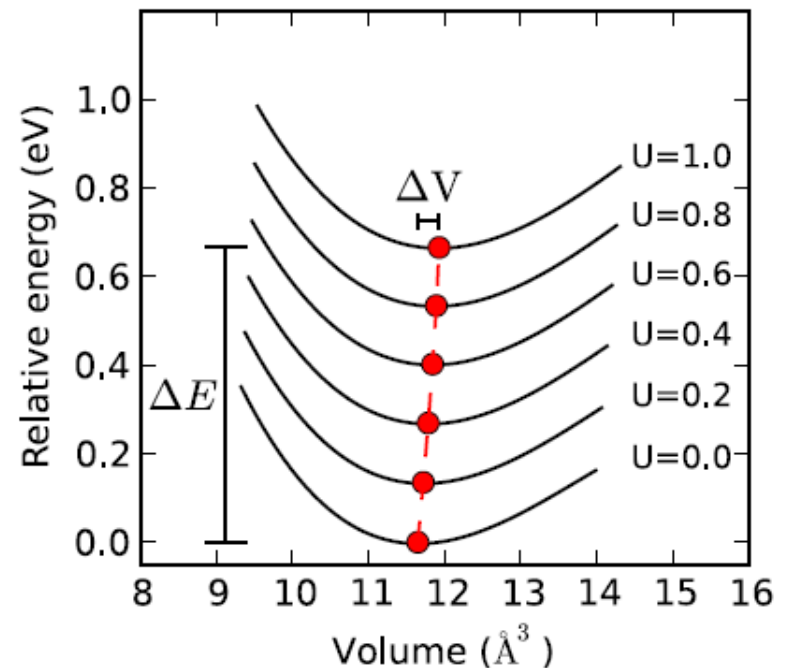
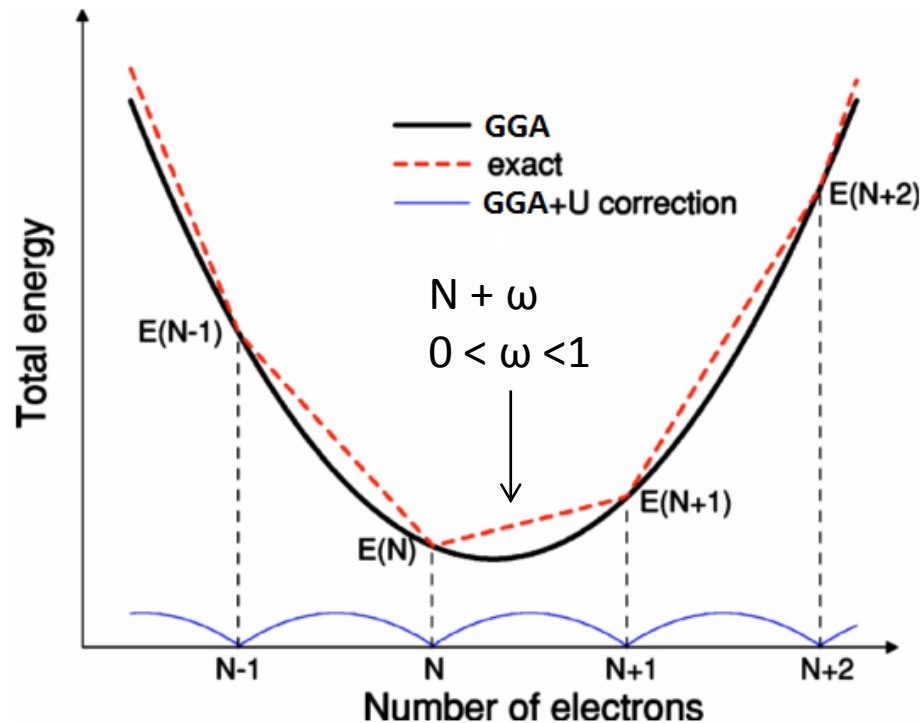
Comparing total energies with different Hubbard U values

- Applying the Hubbard U produces a shift in the total energy that is dependent on the magnitude of the U
- Direct comparisons of total energy between different U values is meaningless \rightarrow like comparing total energies of different exchange correlation functionals



- Researchers usually pick a single, element specific U value for all systems in their study
- The question remains \rightarrow *how does one pick this U ?*

Motivation for empirical usage of the Hubbard U



- Though the formalism of the Hubbard U suggests a material specific U , the arbitrary offset often necessitates a single U for studies
- This Hubbard U is often fit to experimental results

Fixing hole localization with the Hubbard U : Al doped SiO_2

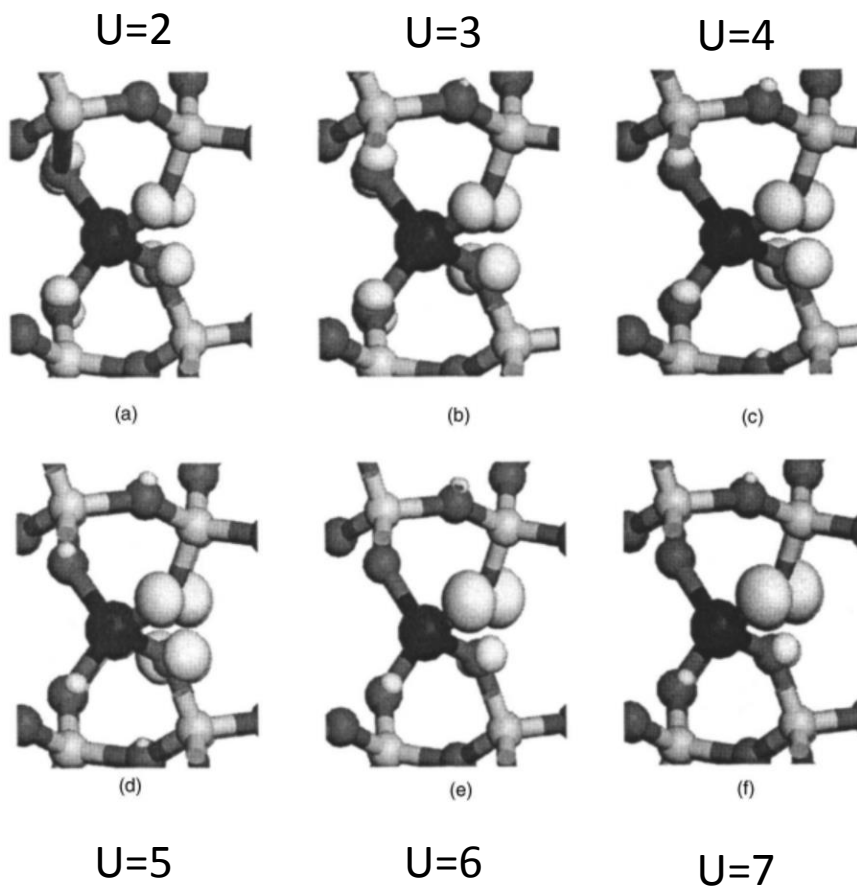
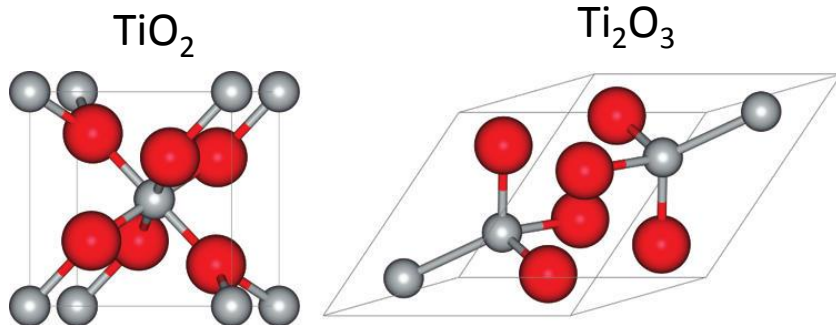


TABLE I. Al–O distances in Al doped silica as a function of U . For the GGA calculation, $U=0$ eV.

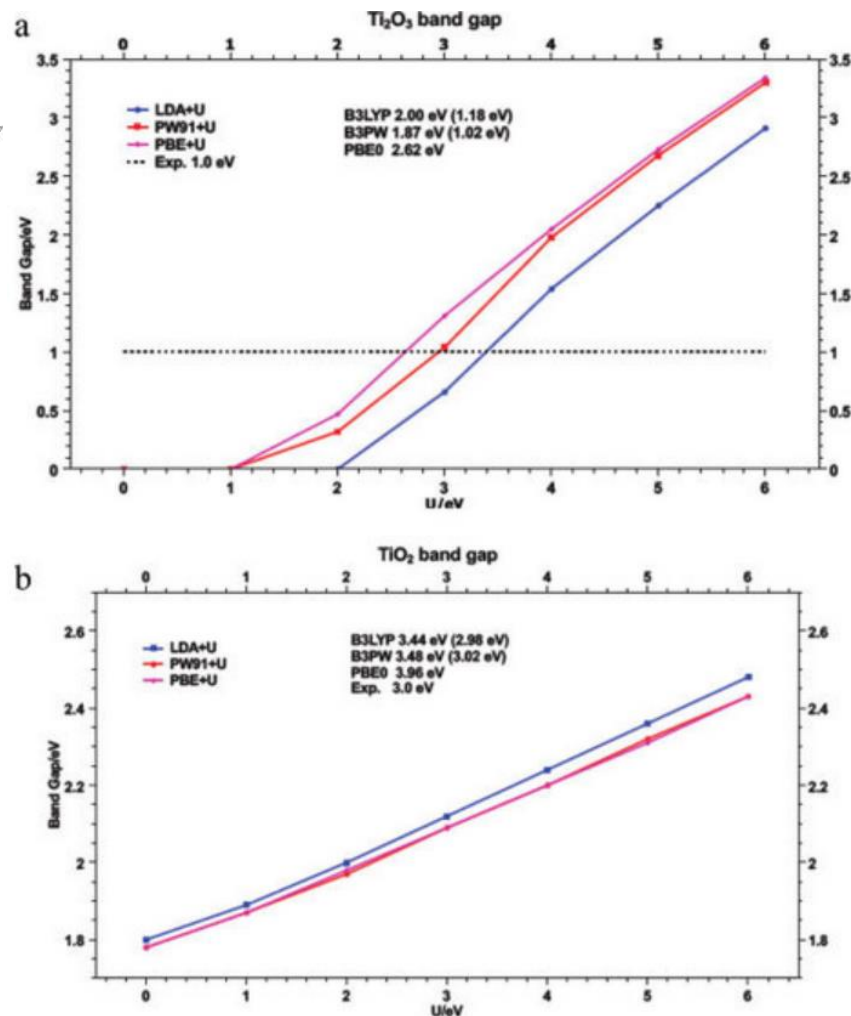
U eV	Al–O distances (Å)
GGA	$2 \times 1.75, 2 \times 1.73$
2	$2 \times 1.75, 2 \times 1.73$
3	$2 \times 1.75, 2 \times 1.72$
4	$2 \times 1.76, 2 \times 1.71$
5	$2 \times 1.76, 2 \times 1.71$
6	1.85, 1.72, 2×1.69
7	1.88, 1.71, 2×1.69

- Applying the U correctly localizes the hole on one bond
- Study empirically picks $U=7$ based on bond lengths compared to experiments

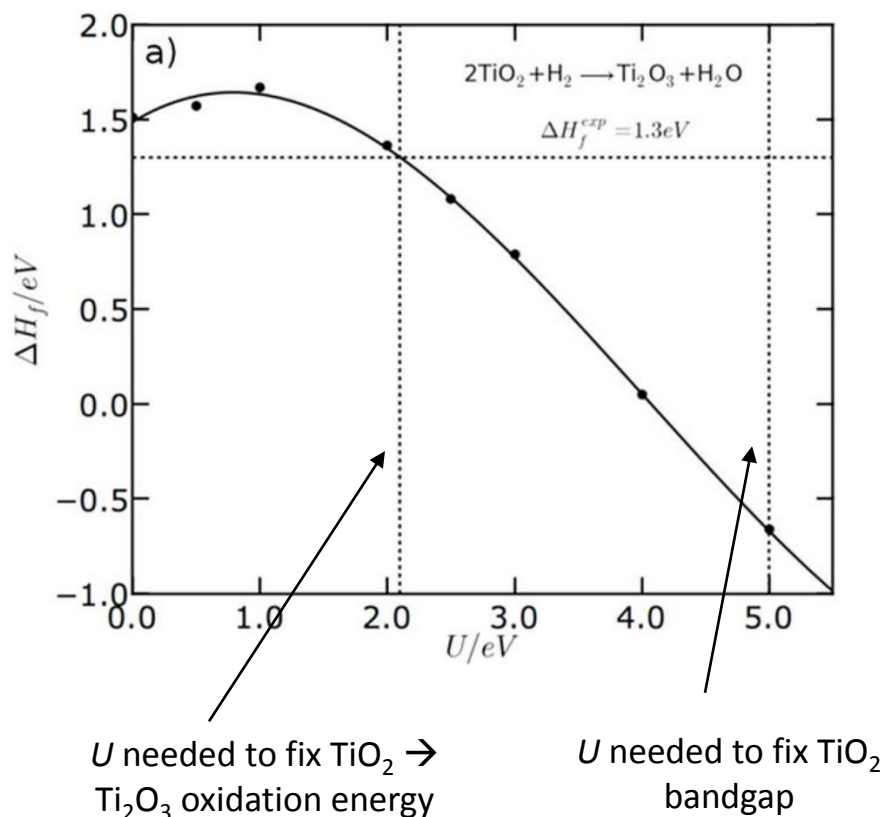
Fixing the band gap of oxides



- Application of U also tends to fix the non-existent of small band gaps of many transition metal oxides
- In this study, found that a different U value is needed for the band gaps of Ti_2O_3 ($U \approx 3$) and TiO_2 ($U \approx 7$)



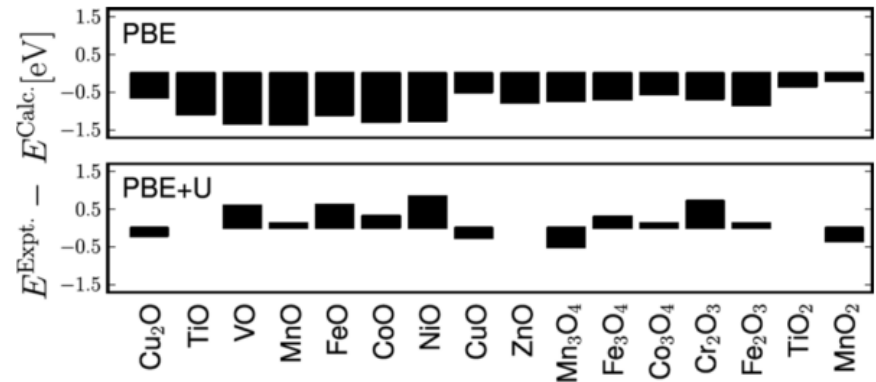
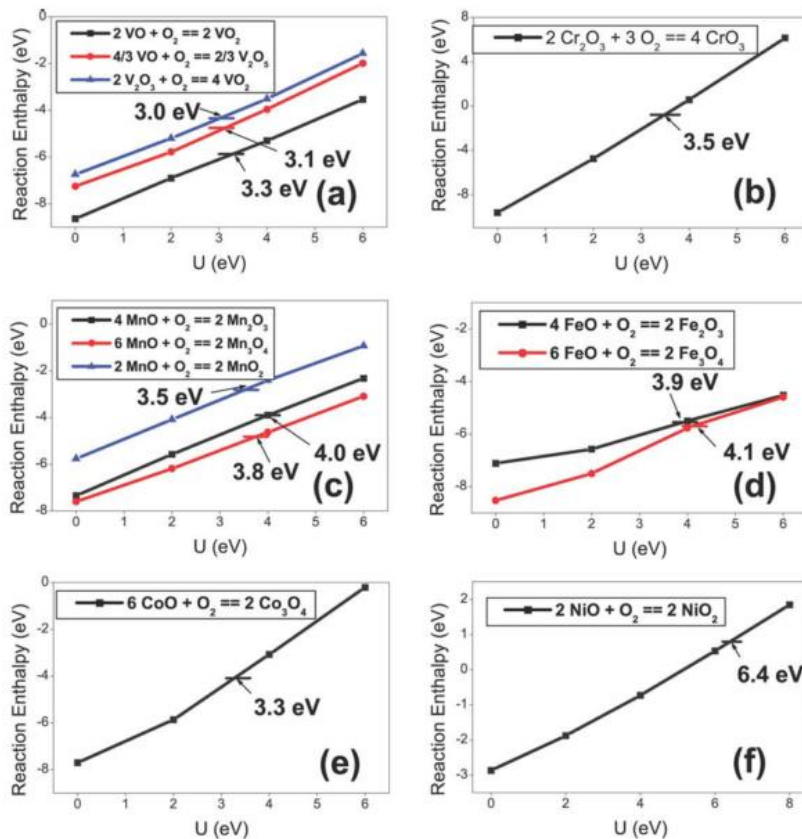
Fixing both electronic structure and thermodynamics?



- In most cases, a single U cannot simultaneously fix both the electronic structure and thermodynamics
- How then does one empirically use the Hubbard U for catalysis amidst these observations?

Fixing oxidation energies with DFT+*U*

- Errors in oxidation energies caused by non-cancellation of error in *d*-orbitals can be fixed by applying Hubbard *U*



Yan, J., & Nørskov, J. K. (2013). Calculated formation and reaction energies of 3*d* transition metal oxides using a hierarchy of exchange-correlation functionals. *Physical Review B*, 88(24), 245204.

- Clear that no single, element *U* can fix all relative stabilities of a single transition metal in multiple oxidation states



Central issues with the empirical approach of picking the Hubbard U

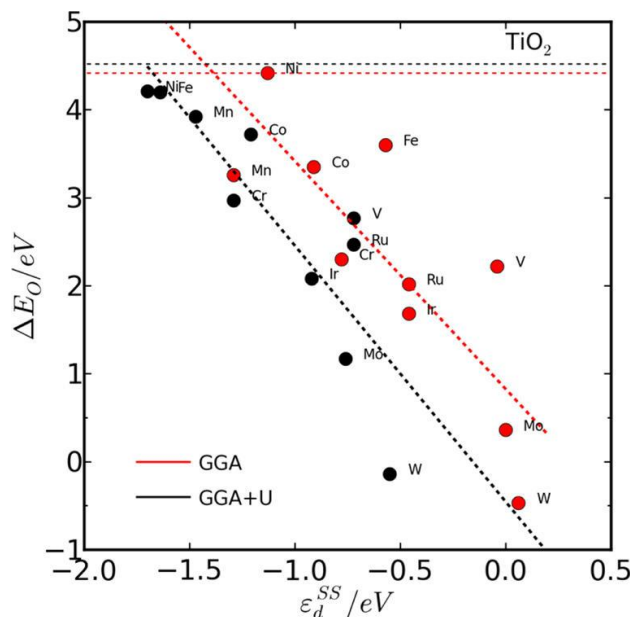
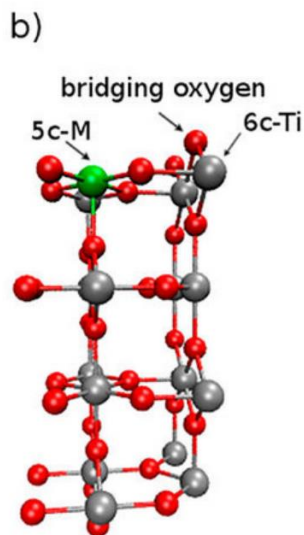
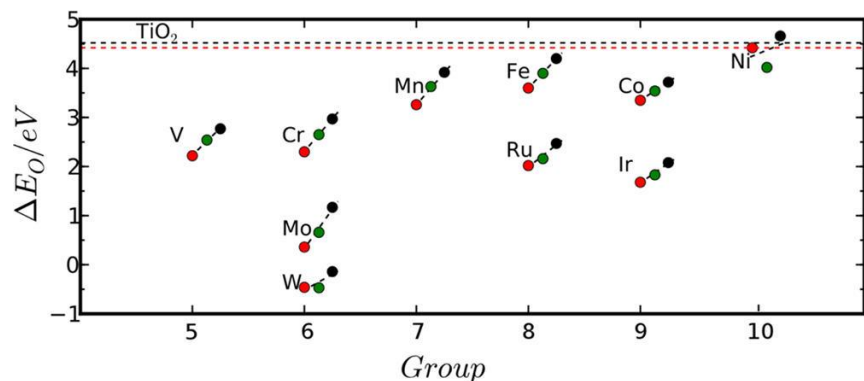
Issues to consider...

- No single, element specific U captures all oxidation energies and electronic structure features of the element in all environments (metal, oxide, etc)
- Does fitting a U one piece of experimental data make it suitable for your current calculation?

Example questions

- Are U 's fitted to bulk oxidation values appropriate when applied to the surface? Adsorption?
- What value of U do you use in mixed oxide systems?
- How do you choose U for predicting relative stabilities of new systems?

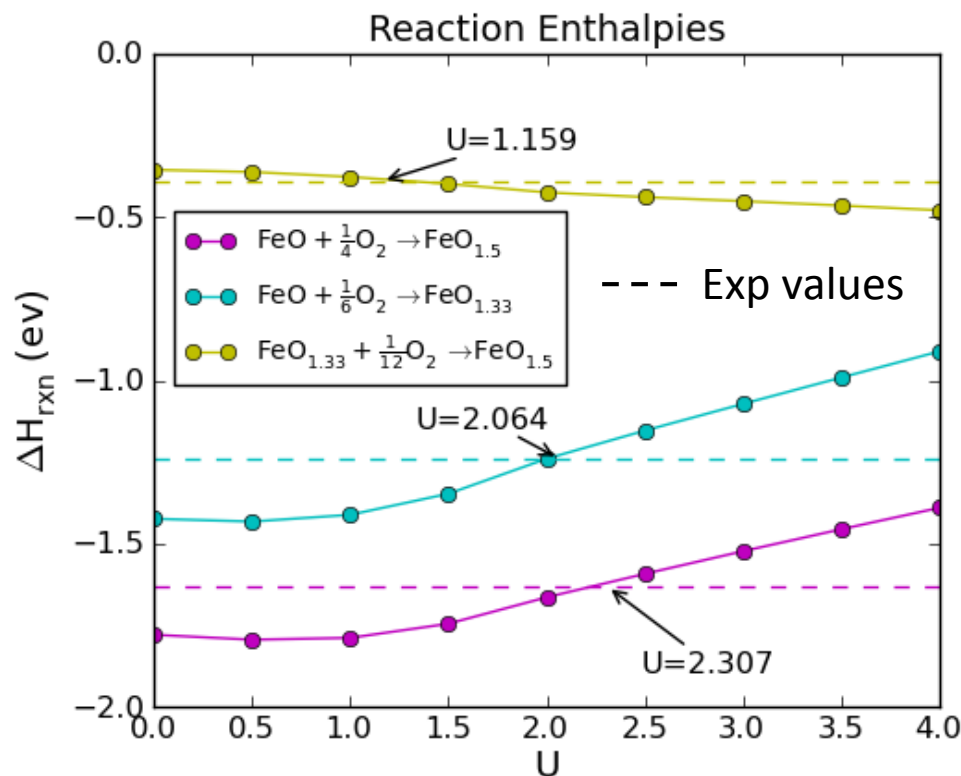
Testing conclusions at several U values



- Evaluate trends at multiple Hubbard U values
- Trends in adsorption energies on doped- TiO_2 hold for $U = 1$ and $U = 2$
- Found a linear change in change in adsorption energy with U
- However, unclear if the same U should be applied to all elements
- Also found electronic structure correlation was independent of the U used

Many researchers resort to performing calculations at multiple U s and seeing if the trends hold

Using bulk oxidation to predict a reaction specific U



- Applying 'U' corrects for all oxidation reactions
- How do we apply this knowledge to select a U for adsorption reactions?
- We need a descriptor that can guide is in picking a 'U' for new reactions

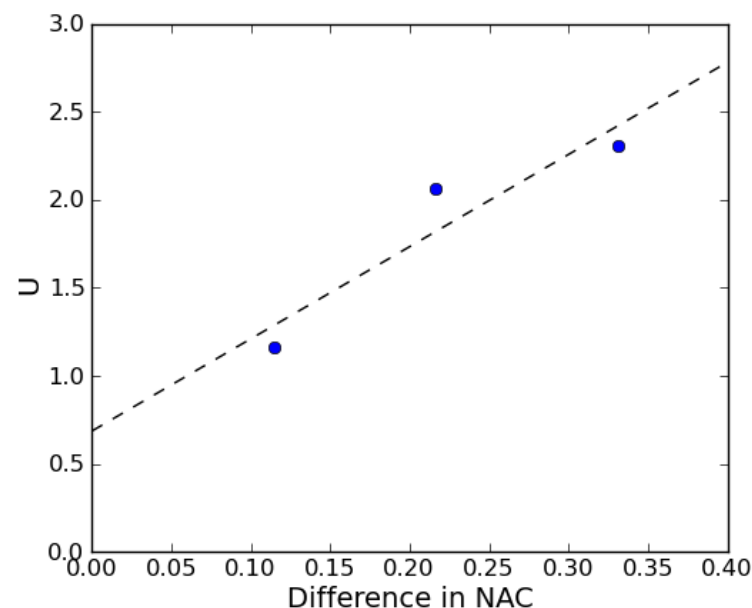
Correlating 'U' and Charge Transfer

Reaction	Oxidation State Change	U needed
$\text{FeO}_{1.33} + \frac{1}{12}\text{O}_2 \rightarrow \text{FeO}_{1.5}$	+0.3	1.16
$\text{FeO} + \frac{1}{6}\text{O}_2 \rightarrow \text{FeO}_{1.33}$	+0.7	2.06
$\text{FeO} + \frac{1}{4}\text{O}_2 \rightarrow \text{FeO}_{1.5}$	+1	2.31

- The amount of 'U' needed seems correlated to amount of charge transfer during the reaction

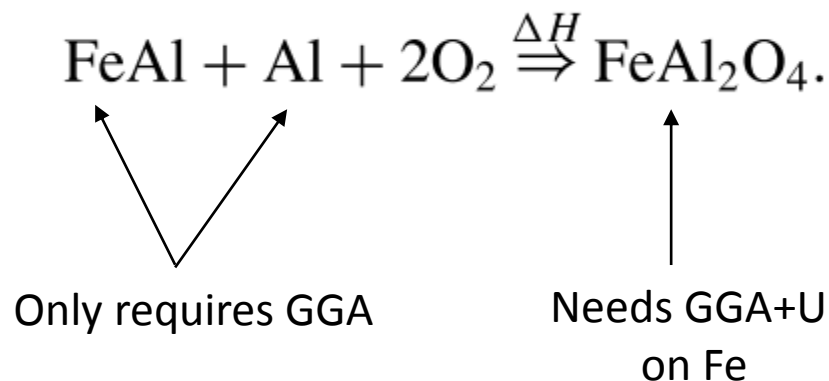
- A measurable value of charge density is the net atomic charge (NAC)
- Calculated using density derived electrostatic and chemical (DDEC) charges

Compound	DDEC NAC of Fe
FeO	+1.41
Fe_3O_4	+1.62
Fe_2O_3	+1.74



Formation enthalpies by mixing GGA and GGA + U calculations

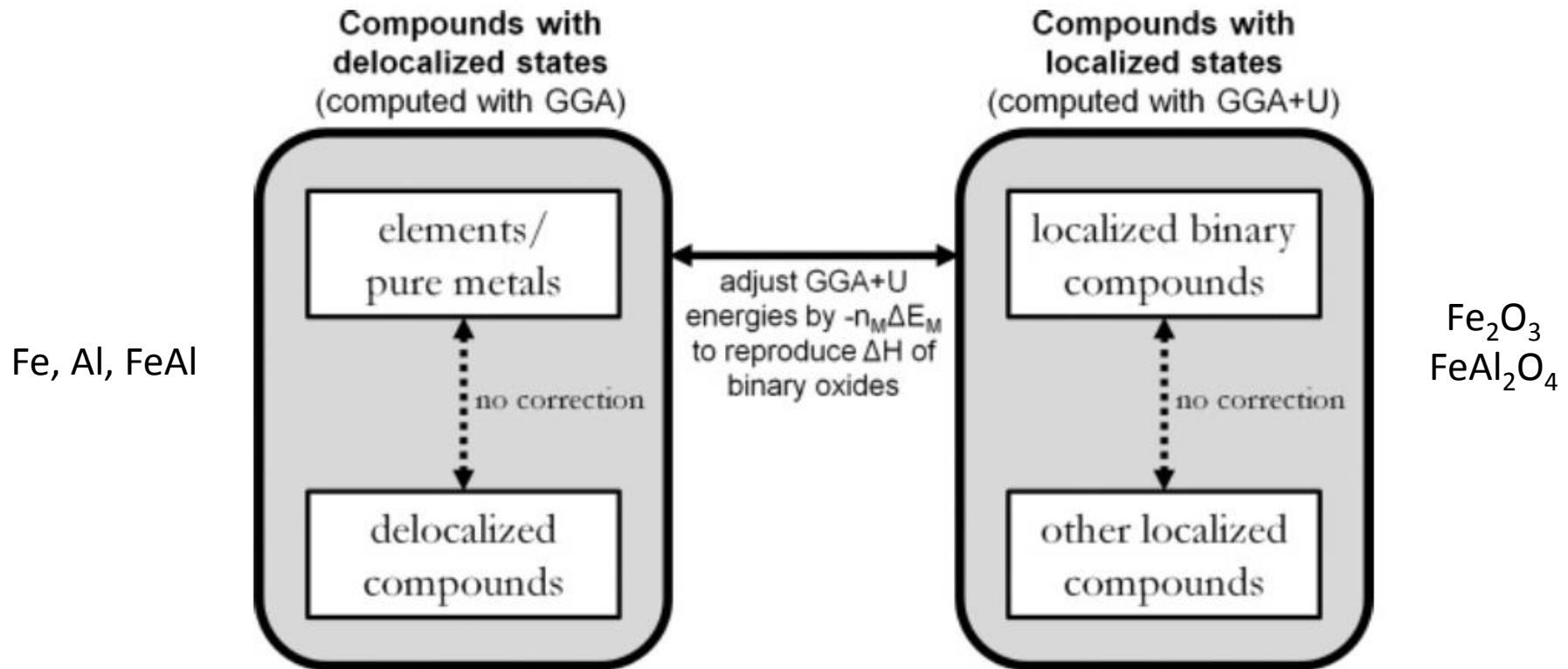
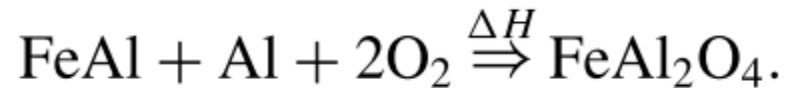
- Accurate formation energies crucial for using DFT in materials discovery
- How do you use the Hubbard U to predict accurate formation energies of mixed oxides?
- The approach from Ceder at MIT...



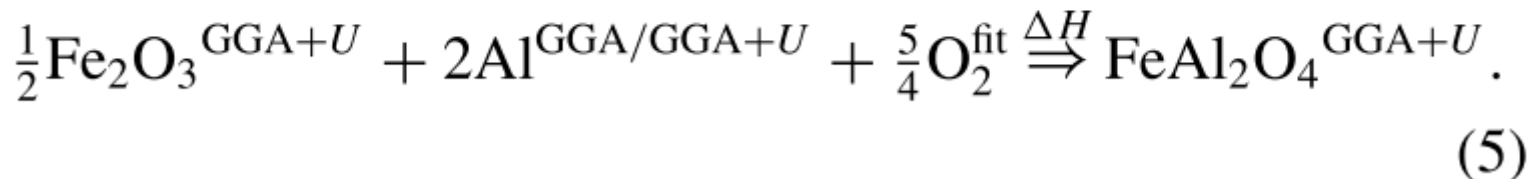
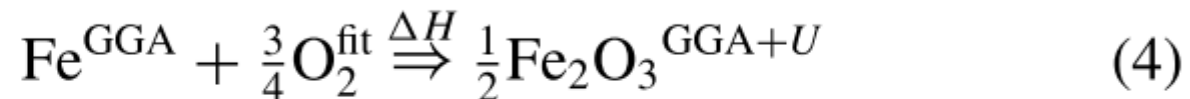
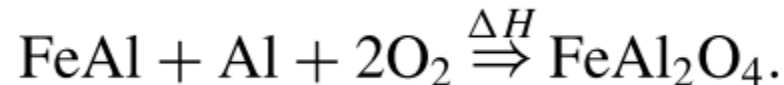
- Needs some way to 'mix' GGA and GGA+U calculations and avoid the error introduced

Formation enthalpies by mixing GGA and GGA + U calculations

- Schemed a strategy to mix GGA and GGA+U calculations

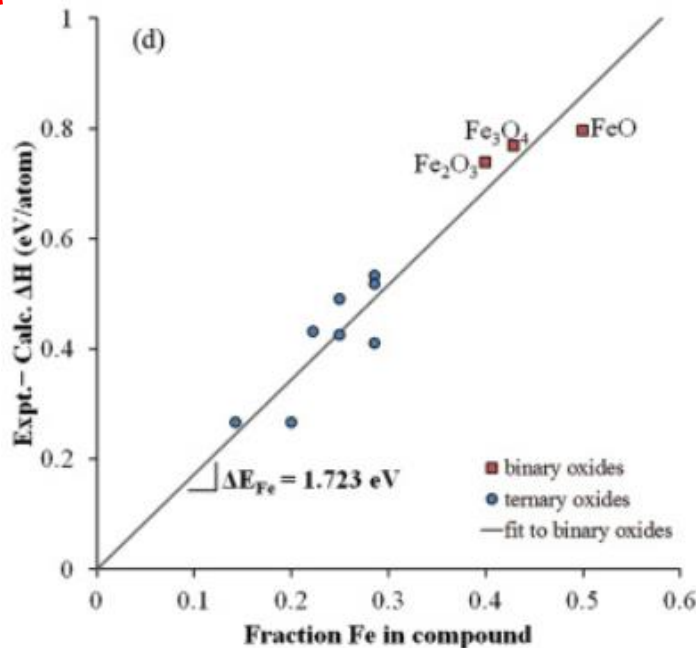
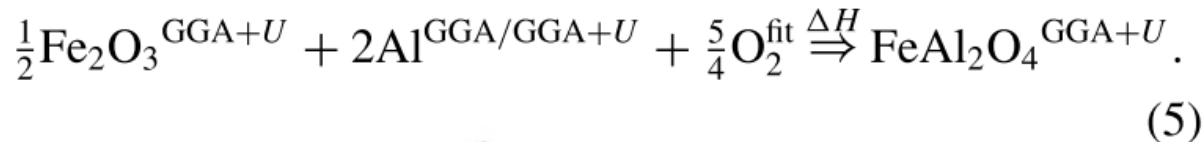
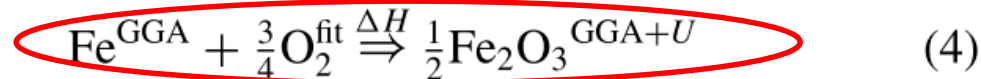


Formation enthalpies by mixing GGA and GGA + U calculations



- Break up the reaction into segments that either only need GGA or GGA+U
- Place oxidation reactions that require GGA+U into a pure oxidation reaction with a known oxidation energy

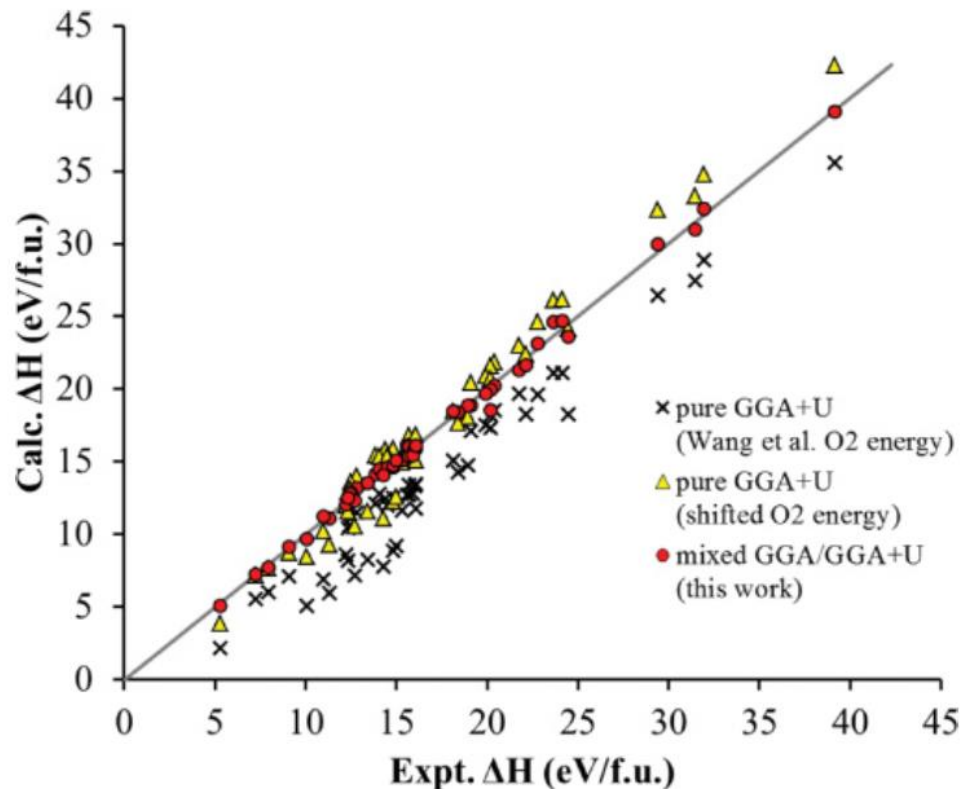
Formation enthalpies by mixing GGA and GGA + U calculations



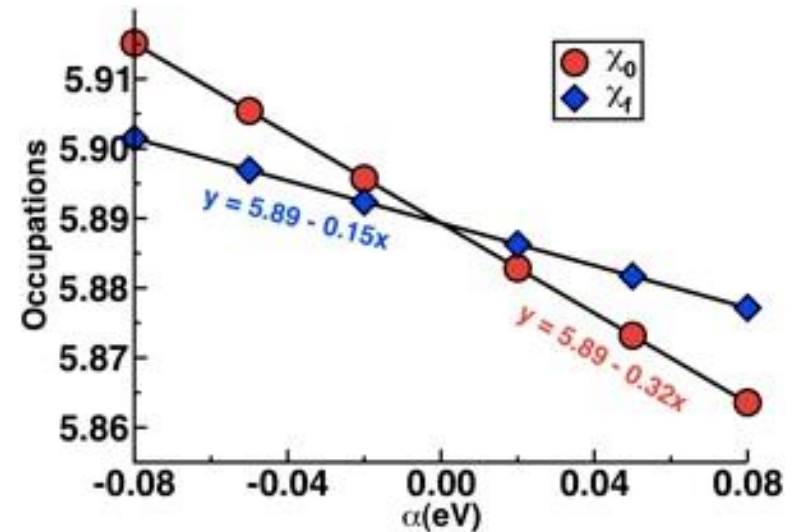
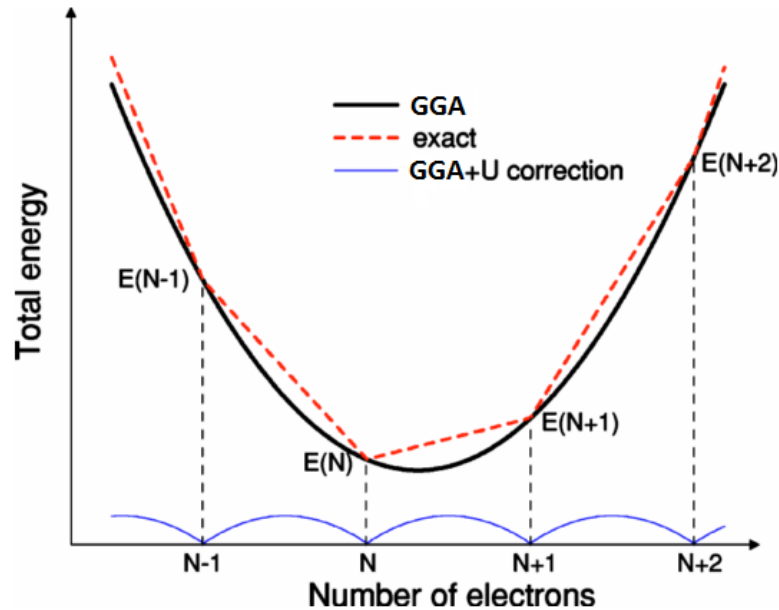
- Found that error in relative stability between metal GGA and oxide GGA+U varies linearly with oxidation state
- Applied empirical correction that depends on the oxidation state of the metal
- Found that errors between metal GGA and mixed oxide GGA+U also lie on this correction line

Formation enthalpies by mixing GGA and GGA + U calculations

- Mixing GGA and GGA+U gave heavily improved results of formation energies of mixed compounds



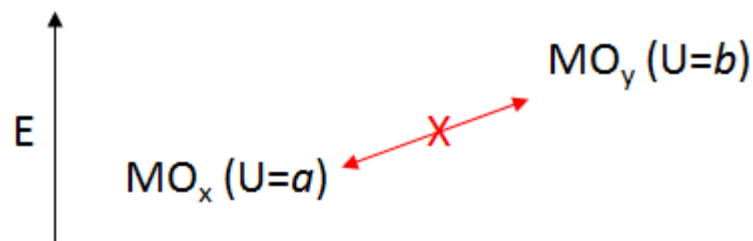
Calculating the Hubbard U



<http://www.kuliklab.org/content/calculating-hubbard-u>

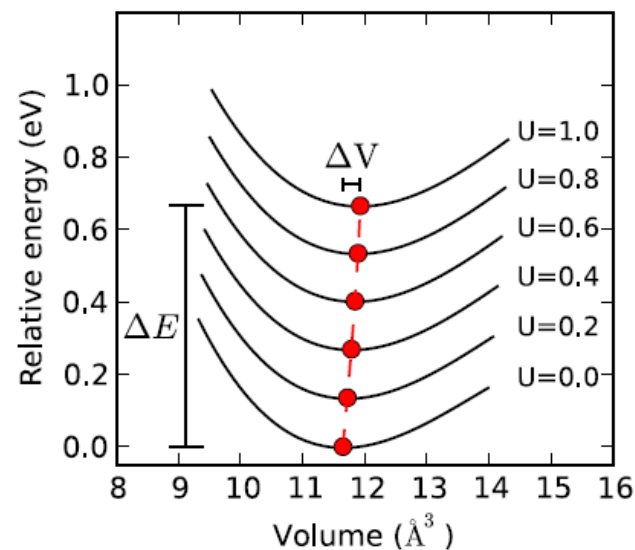
- Material specific Hubbard U related to curvature the total energy with respect to changing occupancies
- Can be calculated via a linear response method
- Slope of perturbation vs occupancies gives information of the curvatures

A method DFT+ $U(\mathbf{V})$ method for comparing energetics with different Hubbard U values



$$\Delta E = \int_{\mathbf{V}} \frac{dE}{d\mathbf{V}} d\mathbf{V} = \int_{\mathbf{V}} \left(\frac{\partial E}{\partial \mathbf{V}} + \frac{\partial E}{\partial U} \frac{dU}{d\mathbf{V}} \right) d\mathbf{V}$$

- The energy difference between two structures at two different U values can be written as a total derivative
- Derivative contains some arbitrary offset which makes the comparison meaningless



- In above example, correct energy difference can be attained by subtracting the $\int_{\mathbf{V}} \frac{\partial E}{\partial U} \frac{dU}{d\mathbf{V}} d\mathbf{V}$ term
- We call $\Delta E = \int_{\mathbf{V}} \frac{\partial E}{\partial \mathbf{V}} d\mathbf{V}$ the DFT+ $U(\mathbf{V})$ energy

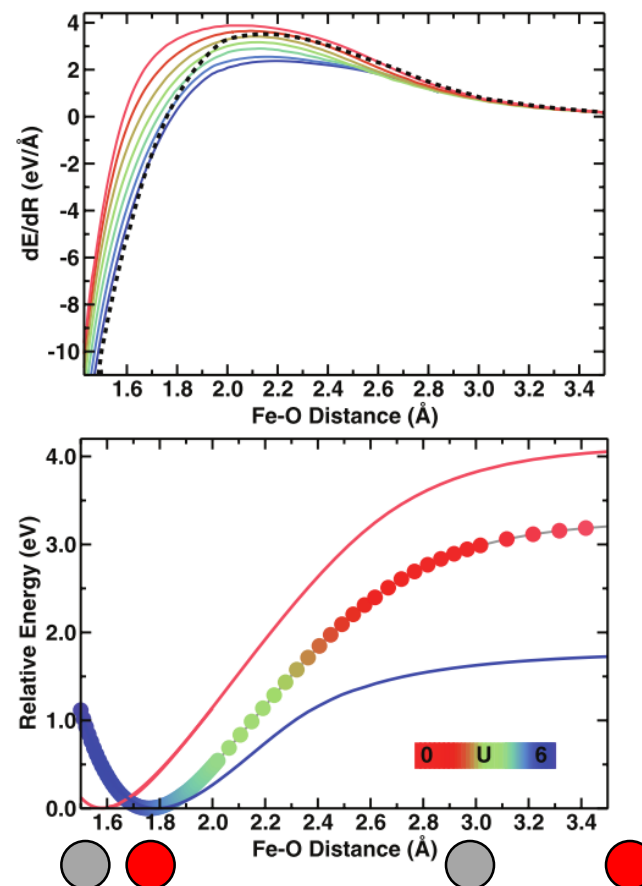
How do we use and validate this method for TMOs?

Requirements of the DFT+ $U(\mathbf{V})$ method:

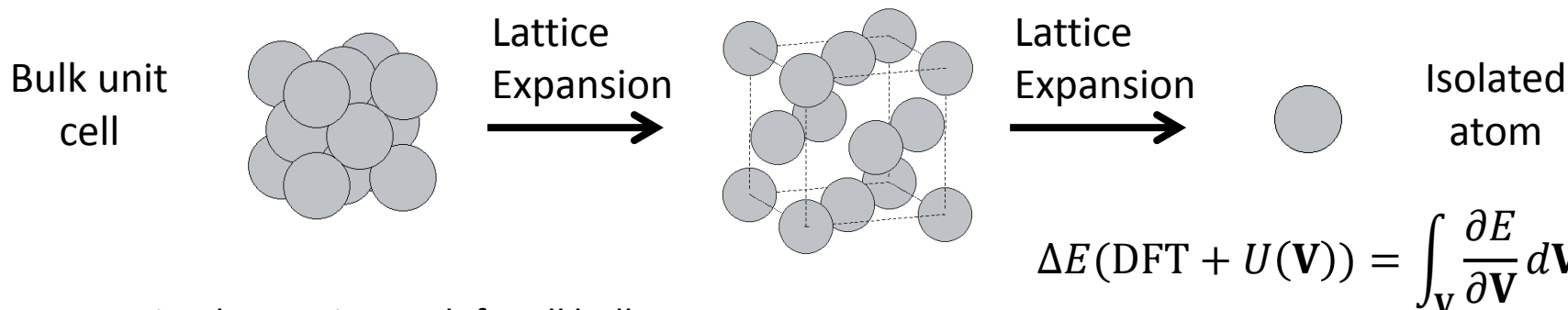
The $U(\mathbf{V})$ relationship

$$\Delta E(\text{DFT} + U(\mathbf{V})) = \int_{\mathbf{V}} \frac{\partial E}{\partial \mathbf{V}} d\mathbf{V}$$

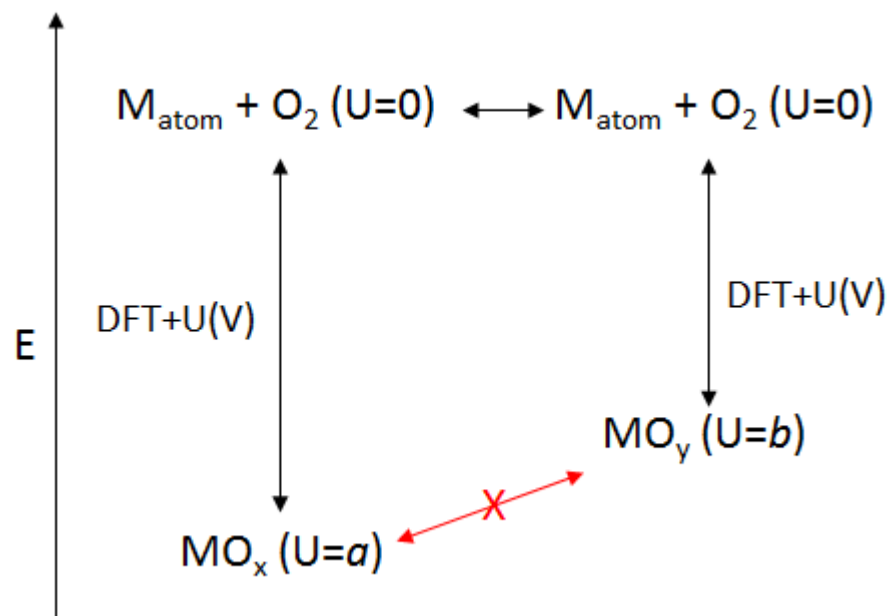
- This method requires both a **reaction path** and $U(\mathbf{V})$ relationship to perform the DFT+ $U(\mathbf{V})$ method over
- Heather Kulik previously used a similar method to obtain more accurate dissociation energies
- Called DFT+ $U(\mathbf{R})$, where reaction path was the simple bond dissociation and the $U(\mathbf{R})$ relationship was the calculated linear response U



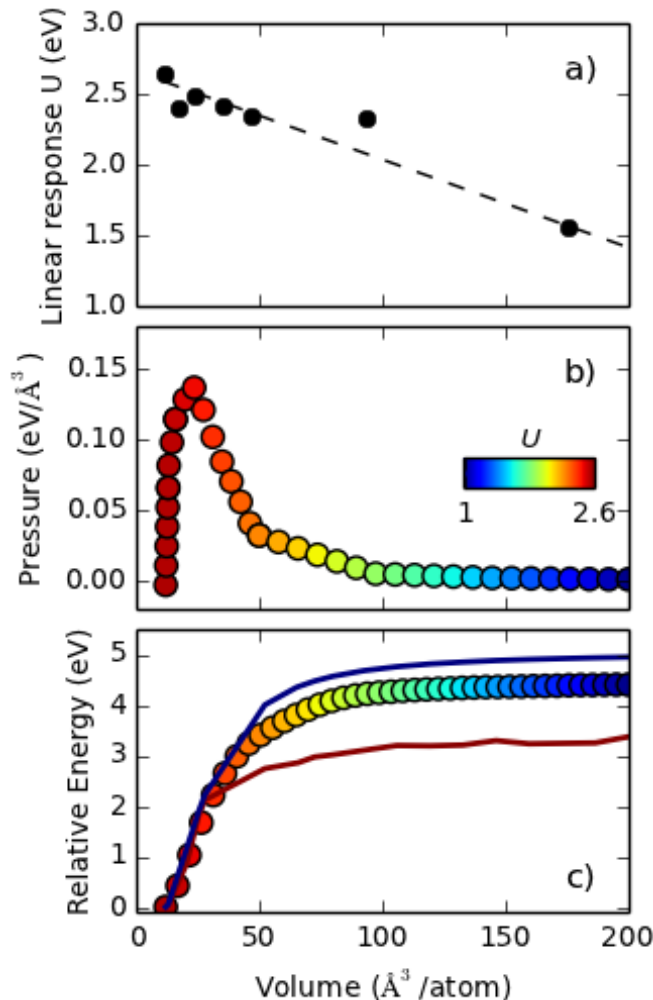
Requirements of DFT+ $U(\mathbf{V})$: A reaction path for bulk materials



- A simple reaction path for all bulk materials is the isotropic expansion of cells
- Can use thermodynamic cycle framework and a common reference to calculate relative stabilities
- The DFT+ $U(\mathbf{V})$ energy is the energy of the bulk material referenced to the isolated atoms



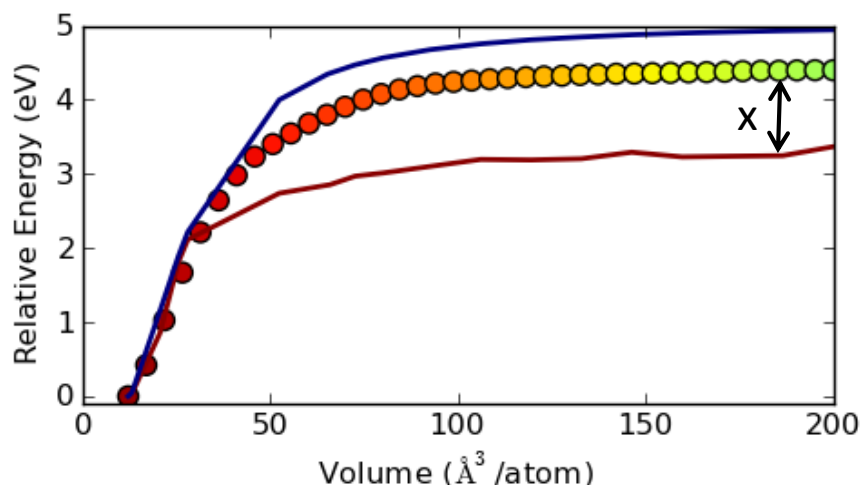
Example DFT+ $U(\mathbf{V})$ Calculation of bulk Fe



$$\Delta E(\text{DFT} + U(\mathbf{V})) = \int_{\mathbf{V}} \frac{\partial E}{\partial \mathbf{V}} d\mathbf{V}$$

- First performed DFT+ $U(\mathbf{V})$ calculation on bulk BCC Fe to test method
- Linear response U decreases with the expansion of the unit cell
- The DFT+ $U(\mathbf{V})$ energy difference is somewhere between the energy difference at $U=0$ and $U=U_{\text{bulk}}$

A Single Empirical Parameter for Estimating DFT+ $U(V)$ Corrected Energy

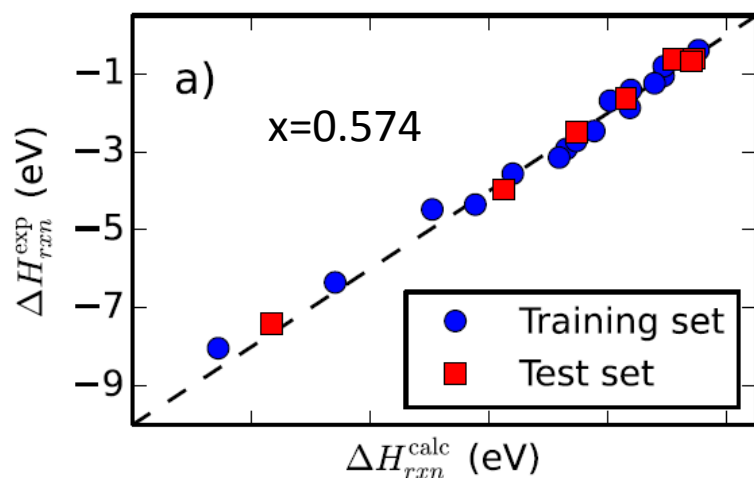


- We expect for all materials, the energy should lie between the U_{bulk} and U_0 energy
- x is a fitting factor that should be material specific depending on the shape of the E vs U curve
- We will **empirically** fit x by minimizing errors in oxidation energies of transition metals and their oxides

Formation Energies	Oxidation Energies
$V \rightarrow VO$	$VO \rightarrow V_2O_5$
$V \rightarrow V_2O_3$	$VO \rightarrow VO_2$
$V \rightarrow VO_2$	$VO \rightarrow V_2O_3$
$V \rightarrow V_2O_5$	$V_2O_3 \rightarrow V_2O_5$
$Fe \rightarrow FeO$	$V_2O_3 \rightarrow VO_2$
$Fe \rightarrow Fe_3O_4$	$VO_2 \rightarrow V_2O_5$
$Fe \rightarrow Fe_2O_3$	$MnO \rightarrow MnO_2$
$Co \rightarrow CoO$	$MnO \rightarrow Mn_3O_4$
$Co \rightarrow Co_3O_4$	$Mn_3O_4 \rightarrow MnO_2$
$Ni \rightarrow NiO$	$FeO \rightarrow Fe_2O_3$
	$FeO \rightarrow Fe_3O_4$
	$Fe_3O_4 \rightarrow Fe_2O_3$
	$CoO \rightarrow Co_3O_4$

Results: Predictive Power of DFT+ $U(V)$

- Split oxidation test reactions into a **training set** and **test set**
- Fit x to training set, and then tested x on the test set



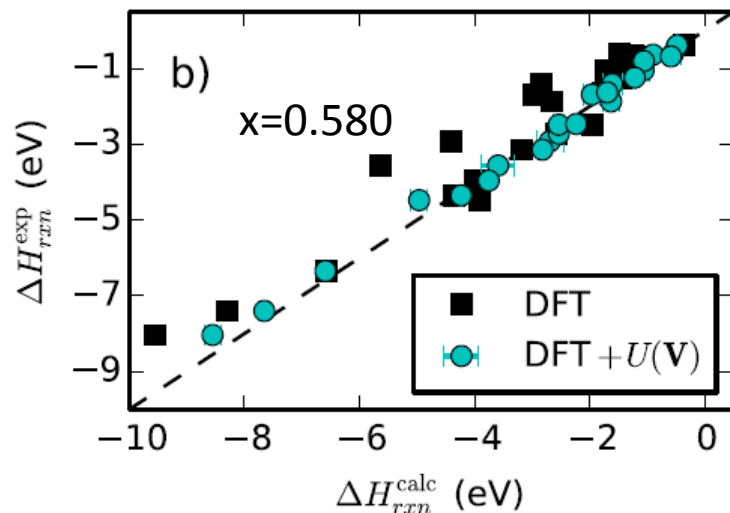
MAE of training set = 0.210 eV/M

MAE of test set = 0.174 eV/M

- Similar MAE demonstrates predictive power of approach

Training Set	Test Set
$\text{V} \rightarrow \text{VO}$	$\text{VO}_2 \rightarrow \text{V}_2\text{O}_5$
$\text{V} \rightarrow \text{V}_2\text{O}_3$	$\text{Mn}_3\text{O}_4 \rightarrow \text{MnO}_2$
$\text{V} \rightarrow \text{V}_2\text{O}_5$	$\text{FeO} \rightarrow \text{Fe}_2\text{O}_3$
$\text{Fe} \rightarrow \text{FeO}$	$\text{V} \rightarrow \text{VO}_2$
$\text{Fe} \rightarrow \text{Fe}_2\text{O}_3$	$\text{Fe} \rightarrow \text{Fe}_3\text{O}_4$
$\text{Co} \rightarrow \text{CoO}$	$\text{CoO} \rightarrow \text{Co}_3\text{O}_4$
$\text{Co} \rightarrow \text{Co}_3\text{O}_4$	$\text{Ni} \rightarrow \text{NiO}$
$\text{VO} \rightarrow \text{V}_2\text{O}_5$	$\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3$
$\text{VO} \rightarrow \text{VO}_2$	
$\text{VO} \rightarrow \text{V}_2\text{O}_3$	
$\text{V}_2\text{O}_3 \rightarrow \text{V}_2\text{O}_5$	
$\text{V}_2\text{O}_3 \rightarrow \text{VO}_2$	
$\text{MnO} \rightarrow \text{MnO}_2$	
$\text{MnO} \rightarrow \text{Mn}_3\text{O}_4$	
$\text{FeO} \rightarrow \text{Fe}_3\text{O}_4$	

Results: Accuracy of DFT+U(V)



- Fit x to all reaction energies and tested the overall accuracy of the approach
- The overall MAE of the DFT+U(V) approach is 0.195 eV/M, compared to 0.657 eV/M with DFT

Formation Energies	Oxidation Energies
$V \rightarrow VO$	$VO \rightarrow V_2O_5$
$V \rightarrow V_2O_3$	$VO \rightarrow VO_2$
$V \rightarrow VO_2$	$VO \rightarrow V_2O_3$
$V \rightarrow V_2O_5$	$V_2O_3 \rightarrow V_2O_5$
$Fe \rightarrow FeO$	$V_2O_3 \rightarrow VO_2$
$Fe \rightarrow Fe_3O_4$	$VO_2 \rightarrow V_2O_5$
$Fe \rightarrow Fe_2O_3$	$MnO \rightarrow MnO_2$
$Co \rightarrow CoO$	$MnO \rightarrow Mn_3O_4$
$Co \rightarrow Co_3O_4$	$Mn_3O_4 \rightarrow MnO_2$
$Ni \rightarrow NiO$	$FeO \rightarrow Fe_2O_3$
	$FeO \rightarrow Fe_3O_4$
	$Fe_3O_4 \rightarrow Fe_2O_3$
	$CoO \rightarrow Co_3O_4$

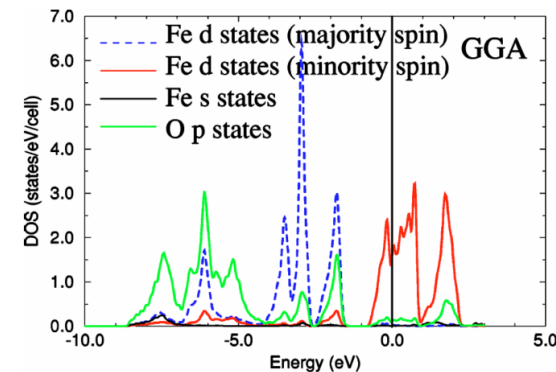
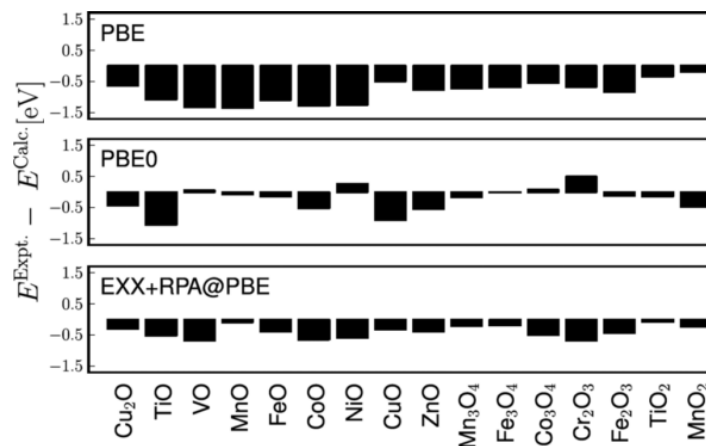
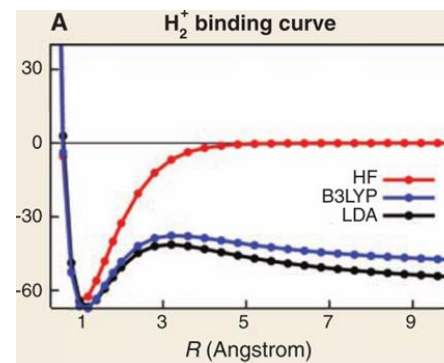
Summary: Source of self-interaction error

$$\left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \sum_l \frac{Z_l}{|\mathbf{r}_j - \mathbf{R}_l|} + \int \frac{n(\mathbf{r}')}{|\mathbf{r}_j - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(n(\mathbf{r})) \right\} \phi_j = \epsilon_j \phi_j$$

- Self-interaction error present in the electron-electron repulsion of the Kohn Sham equations
- LDA and GGA exchange current functionals do not appropriately account for this

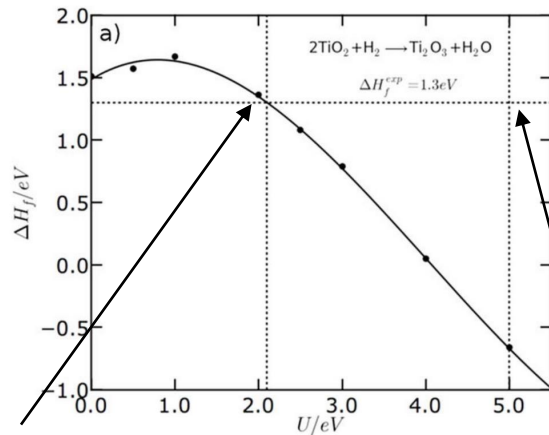
Summary: Effects of self-interaction error

- Self-interaction error often expresses itself as a **delocalization**
- **Electronic structure errors**
 - Hole delocalization
 - Small/non-existent bandgaps
- **Kinetic errors** → low transition states
- **Thermodynamic errors** → Incorrect oxidation energies



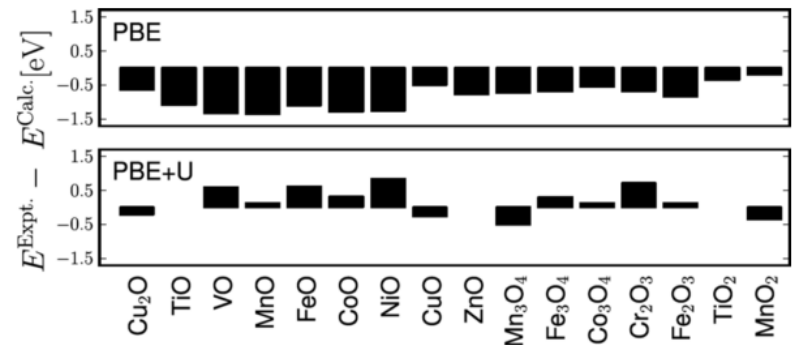
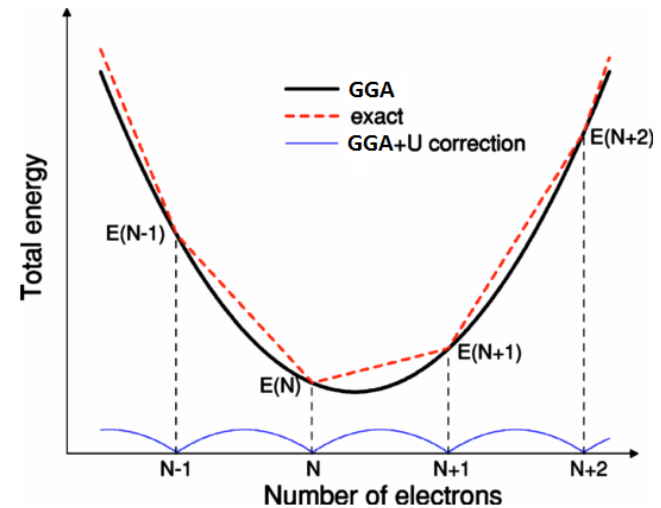
Summary: The Hubbard U

- Computationally cheap and can seemingly fix many errors
- However, no single element specific U can fix *all* errors in the electronic structure and thermodynamics



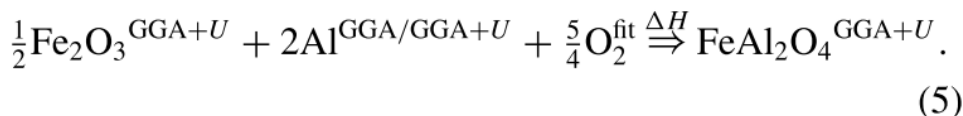
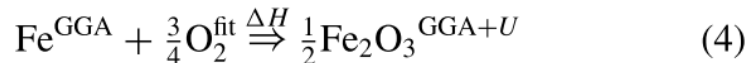
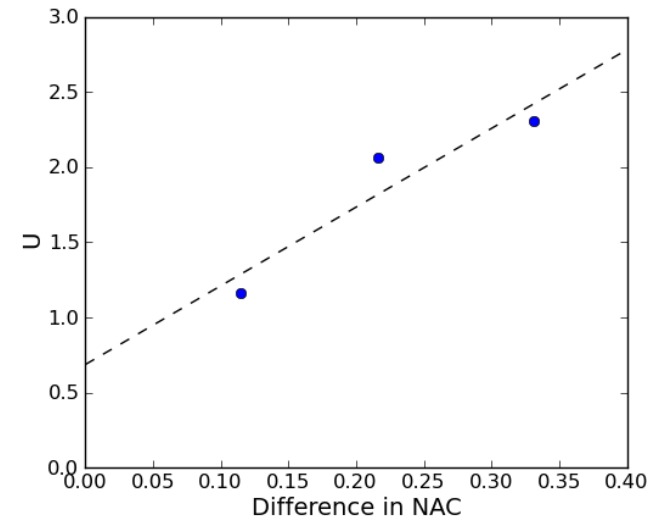
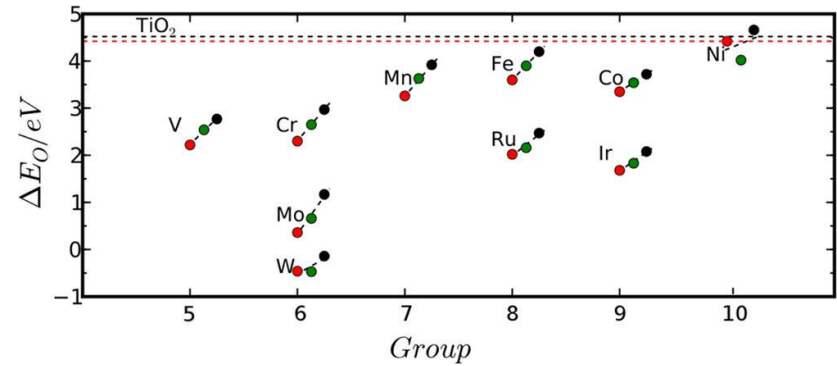
U needed to fix $\text{TiO}_2 \rightarrow$
 Ti_2O_3 oxidation energy

U needed to fix
 TiO_2 bandgap



Summary: Empirical approaches to applying the Hubbard U

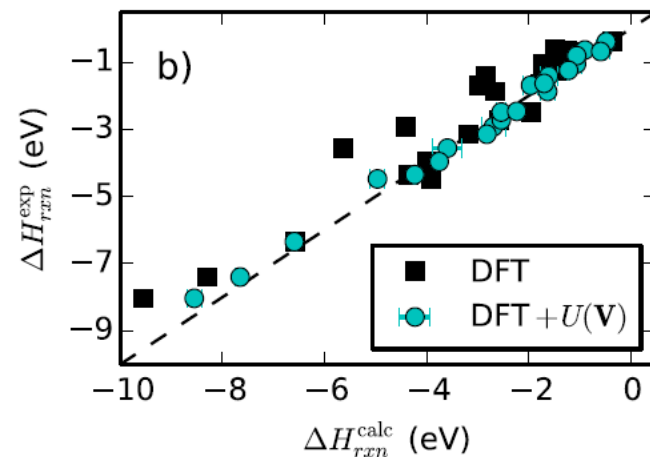
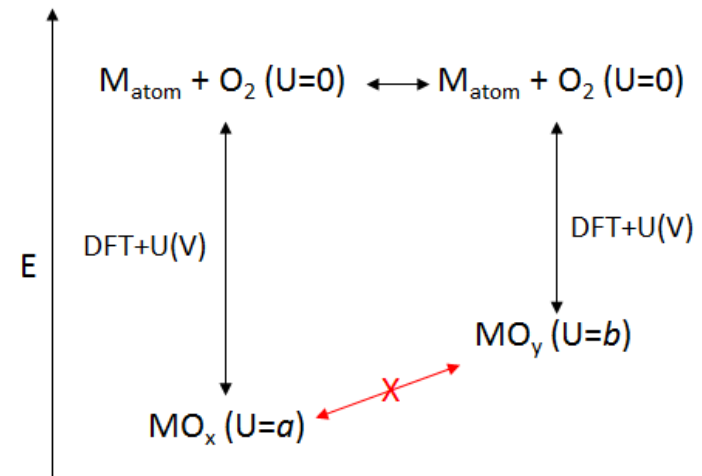
- Several approaches towards empirically applying the U
- Testing conclusions at different U values
- Relating the empirically determined U to chemical properties of the system
- Splitting up reactions and applying an empirical correction



Summary: Applying a calculated linear response U

$$\Delta E(\text{DFT} + U(\mathbf{V})) = \int_{\mathbf{V}} \frac{\partial E}{\partial \mathbf{V}} d\mathbf{V}$$

- Devised a method to eliminate meaningless contributions to total energy at different U values
- Constructed a thermodynamic cycle to easily calculate these contributions
- Found large reductions in the oxidation energy of many 3d transition metal materials



Thank you for listening

Questions?