

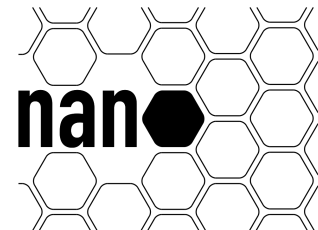
DFT + U: strongly correlated electrons

Guilherme Ribeiro Portugal

guilherme.rportugal@gmail.com

Nanoscience and Advanced Materials (PPG-NMA)

Federal University of ABC – UFABC



Outline

- 1) Correlation
- 2) DFT+U
- 3) Applications
- 4) Final Remarks

Correlation

Correlation interaction

○ Correlation interaction:

- Movement and presence of an e^- influence all other e^- 's
- Electrons repel each other according to Coulomb's law ($\propto \mathbf{r}_{ij}^{-1}$)
- Correlated motion: \downarrow $e^- - e^-$ repulsion

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How should we treat it ?

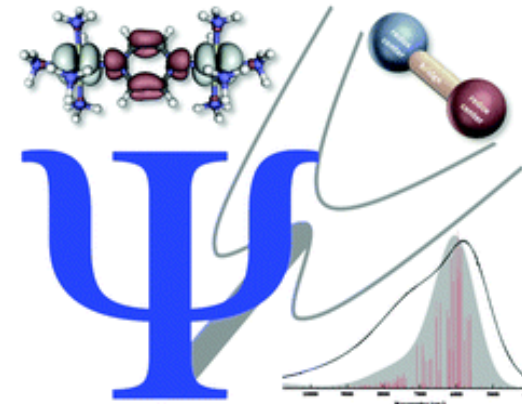
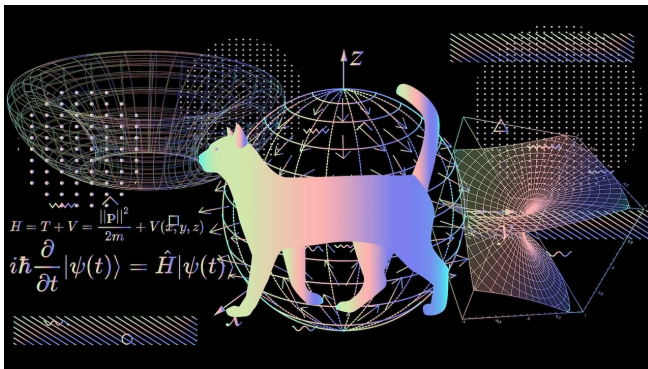
Physicist

vs.

Chemist

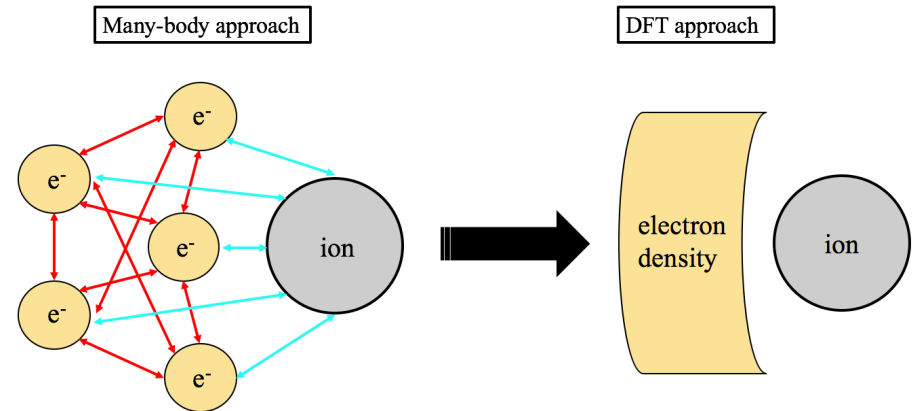
- Atomic-scale Coulomb repulsion and exchange interactions rigorously
- Correlated probability densities of individual electrons

- Dynamic (short-range)
- Static (long-range)



Density Functional Theory

- Born-Oppenheimer approximation
- Hohenberg-Kohn theorems
- Kohn-Sham *ansatz*

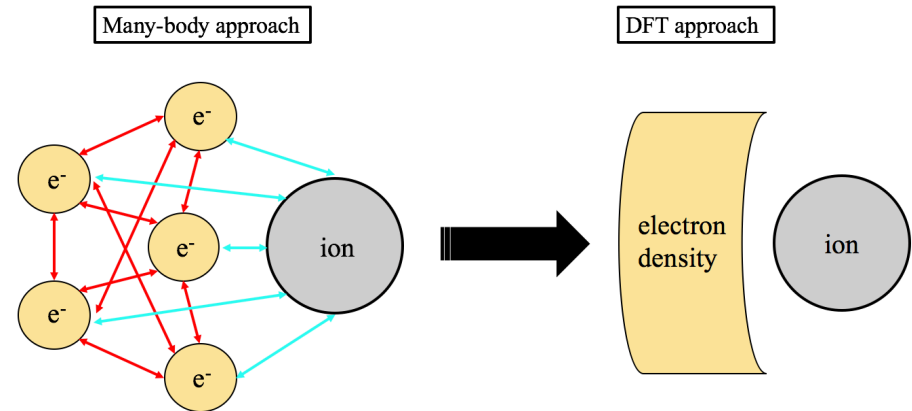


$$\rho(\mathbf{r}) = \sum_{\sigma} \sum_{i=1} |\phi_i^{\sigma}(\mathbf{r})|^2 \quad (1)$$

$$E_{KS} = T_{ni}[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r} + E_{Hartree}[\rho] + E_{add} + E_{xc}[\rho] \quad (2)$$

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$$E_{KS} = \underbrace{T_{ni}[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r} + E_{Hartree}[\rho] + E_{add}}_{\text{Independent particle solvable equations}} + \boxed{E_{xc}[\rho]}_{\text{Exchange-correlation functional}} \quad (2)$$

???

E_{xc} functional - DFT

- Exchange-correlation density functional from Kohn-Sham *ansatz*:

$$E_{xc}[\rho] = \underbrace{\{T_{int}[\rho] - T_{ni}[\rho]\}}_{\text{Kinetic term}} + \underbrace{\{E_{int}[\rho] - E_{Hartree}[\rho]\}}_{\text{Potential term}} \quad (3)$$

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→ Depends on how the density is treated!

- Local density approximation (LDA): homogeneous electron gas – HEG

$$E_{xc}^{LDA}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{xc}[\rho] d^3\mathbf{r} \quad (4)$$

$$E_{xc}[\rho] = E_{exchange} + E_{correlation} \quad (5)$$

- $E_{exchange}$: analytically for a HEG (Dirac exchange)
- $E_{correlation}$: ???

└→ Parameterized equations → Quantum Monte Carlo simulations

- Nowadays...
 - Accurate empirical and semi-empirical approximations for $E_{xc}[\rho(\mathbf{r})]$
 - Mostly based upon corrections in the exchange term
 - Mainly concerned with the bandgap magnitude → great accuracy!

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What about strongly correlated materials ???

- Perturbative correlation expansions (many-body perturbation theory - GW, RPA ...)!

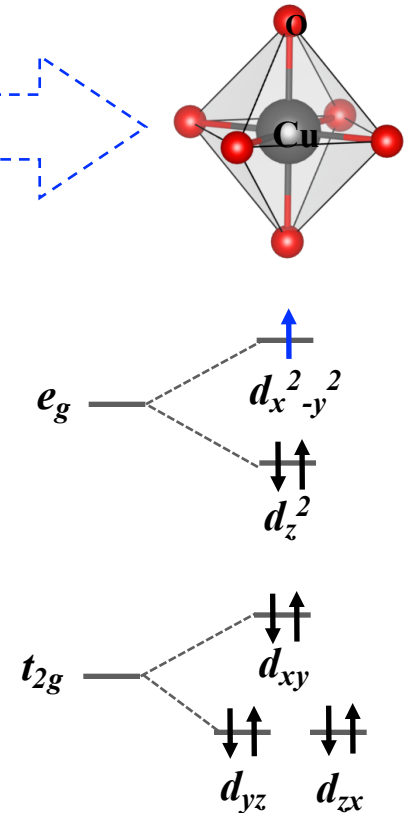
DFT+U

Mott-insulators

- Expected to be conductors by the conventional band theory
- Partially filled d orbitals \rightarrow gapless bands
- Happen to be insulators in the real life!

La_2CuO_4

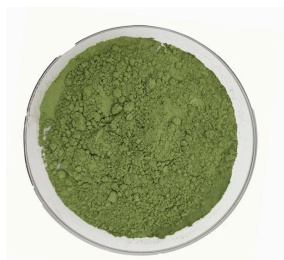
$\text{Cu}^{2+} 3d$ state



Mott-insulators

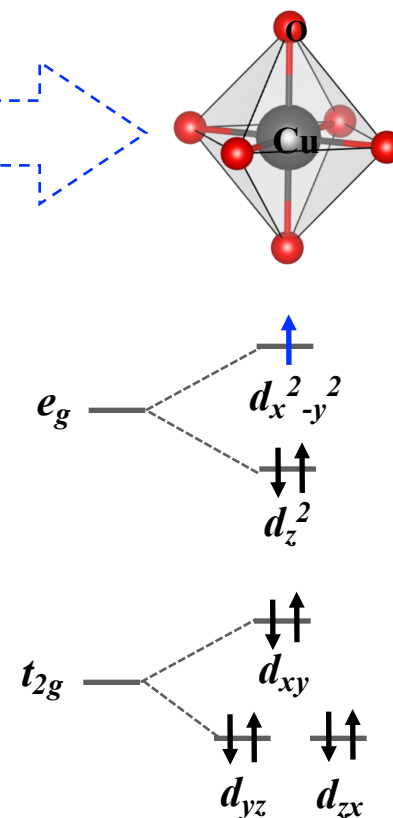
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- NiO, MnO, V_2O_3 , La_2CuO_4 , $LaTiO_3$...



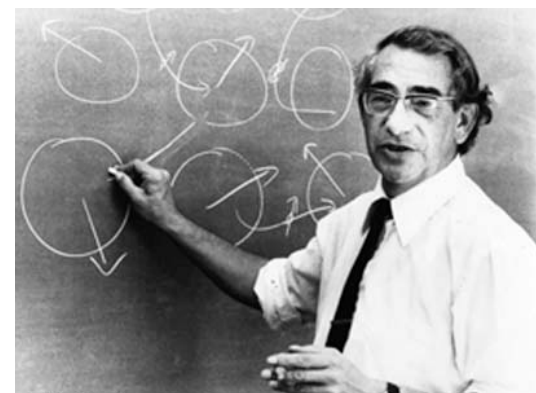
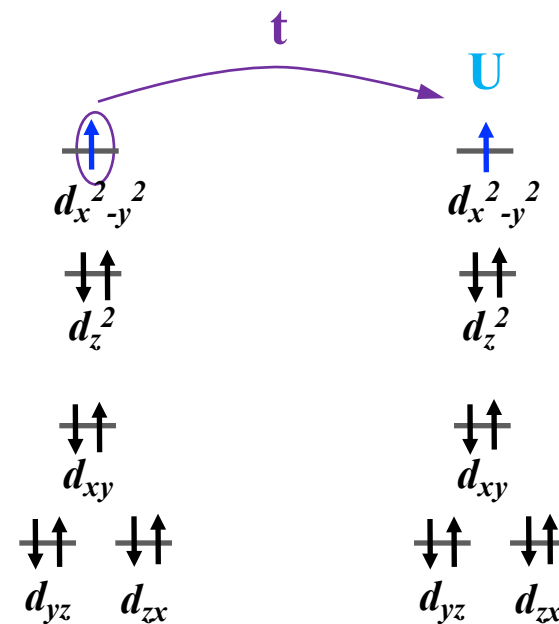
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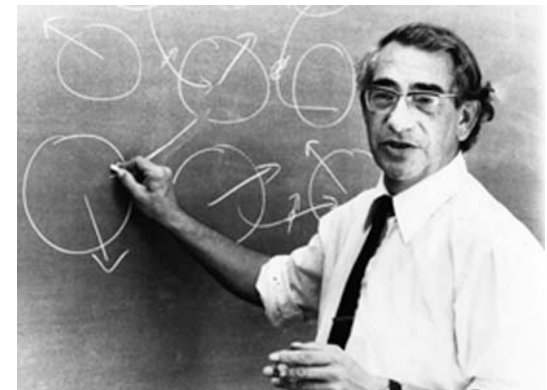
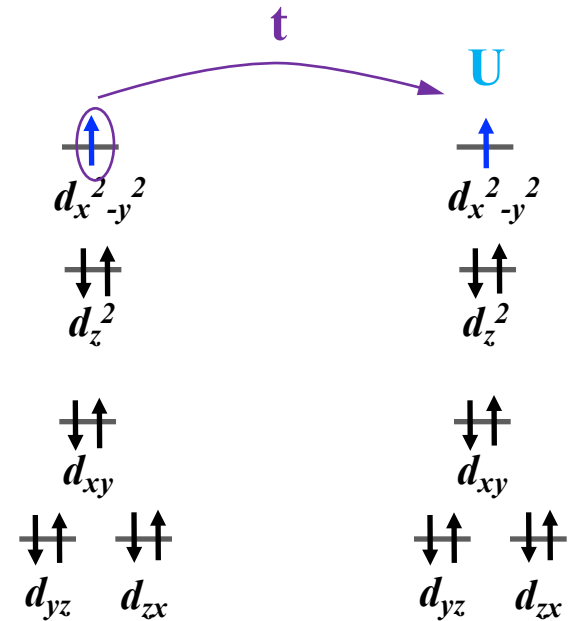
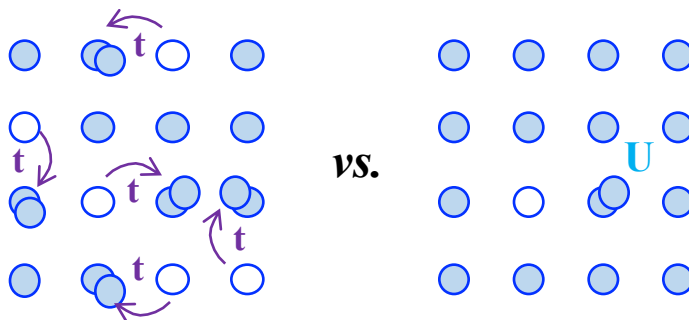
Hubbard model

- Electron transfer integral (t)
- Coulomb $e^- - e^-$ repulsion (U)



Hubbard model

- Electron transfer integral (t)
- Coulomb $e^- - e^-$ repulsion (U)
- Competition: U vs. t
 - U favors localization
 - t favors delocalization



$$H_{Hubbard} = -t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + c_{j,\sigma}^\dagger c_{i,\sigma}) + U \sum_{i=1}^N N^{I\uparrow} N^{I\downarrow} \quad (6)$$

E_k (hopping of e^- 's between nearest neighbors)

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Second quantization notation

$c_{i,\sigma}^\dagger$: creation operator – creates an e^- on atom i with spin σ

$c_{i,\sigma}$: annihilation operator – annihilates an e^- on atom i with spin σ

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On-site onsite $e^- - e^-$ repulsion = Hubbard U (\sim eV)

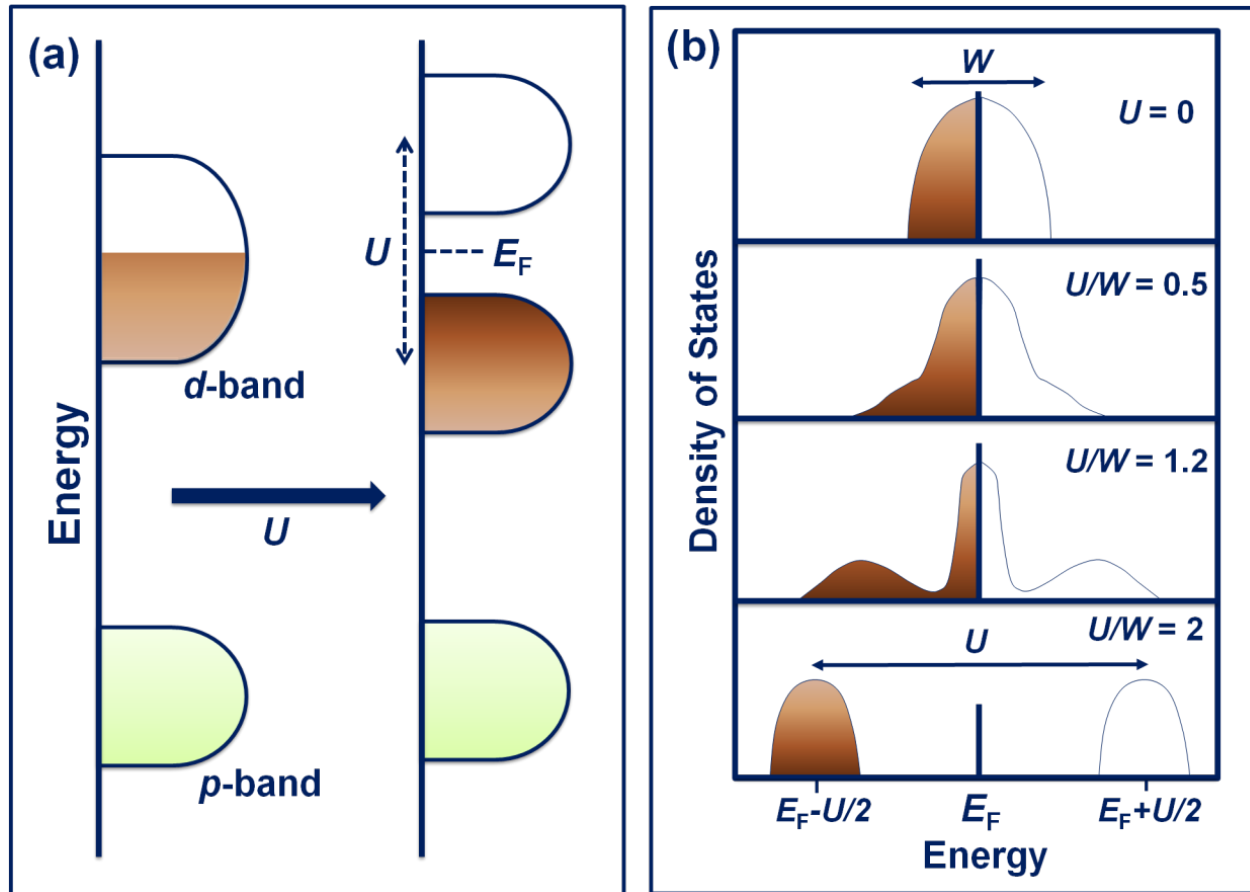
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$N^{I\uparrow}, N^{I\downarrow}$: number of spin up or down e^- 's on each atom $i \rightarrow N^{I,\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma}$

$$W \propto t$$



A. Biswas, K. S. Kim and Y. H. Jeong , *IntechOpen* (2016).

DFT + U

- Main idea consists of adding a repulsive correction term *ad-hoc*
- It separates two subsystems:

DFT + U

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- It separates two subsystems:
 - *s* and *p* electrons (delocalized) → orbital-independent one-electron potentials (LDA, GGAs ...)
 - *d* and *f* electrons (localized) → model Hamiltonian that includes on-site Coulomb interactions

DFT + U

$$E_{DFT+U}[\rho(\mathbf{r})] = E_{DFT}[\rho(\mathbf{r})] + E_{Hub}[(n_{m_l}^{I,\sigma})] \quad (7)$$

- On-site I
- For each magnetic quantum number ml of a given orbital nl

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- For each magnetic quantum number m_l of a given orbital nl

U_{nl}^I → Repulsive interaction

$$\triangleright E_{Hub} = \sum_I \left[\frac{U_{nl}^I}{2} \sum_{m,\sigma \neq m'\sigma'} n_m^{I,\sigma} n_{m'}^{I,\sigma'} \right], \quad n_m^{I,\sigma} : \text{occupation number of the } m^{\text{th}} m_l \text{ state}$$

DFT + U

○ E_{DC} – double-counting term:

- Models the contribution of correlated electrons to the DFT energy as a mean-field approximation of E_{Hub}
- Used to compensate for the correlation energy already contained in the standard DFT Hamiltonian
- No explicit expression of E_{xc} → difficult to model how electronic correlation is accounted for in approximate DFT energy functionals.

- E_{DC} : double-counting term most popular choices:
 - “Around mean-field” (AMF)
 - “Fully localized limit” (FLL)

$$E_{DC}[N_{nl}^{I\sigma}] = \sum_I \left[\frac{U_{nl}^I}{2} N_{nl}^I (N_{nl}^I - 1) - \frac{J^I}{2} \sum_{\sigma} N_{nl}^{I,\sigma} (N_{nl}^{I,\sigma} - 1) \right] \quad (8)$$

U : screened averaged on-site Coulomb repulsive interaction

J : screened averaged exchange term – two e^- 's of parallel spins

$$E_{DFT+U}[\rho(\mathbf{r})] = E_{DFT}[\rho(\mathbf{r})] + E_{Hub}[(n_{m_l}^{I,\sigma})] - E_{DC}[N_{nl}^{I,\sigma}] \quad (9)$$

- Rotationally invariant formulation (most complete);
- Simpler formulation considering $U_{\text{eff}} = U - J$ and $J = 0$ yields:

$$E_{DFT+U} = E_{DFT} + \frac{1}{2} \sum_{I,\sigma} \sum_{nl} U_{nl}^I \left\{ \text{Tr}[\mathbf{n}_{nl}^{I,\sigma} (1 - \mathbf{n}_{nl}^{I,\sigma})] \right\} \quad (10)$$

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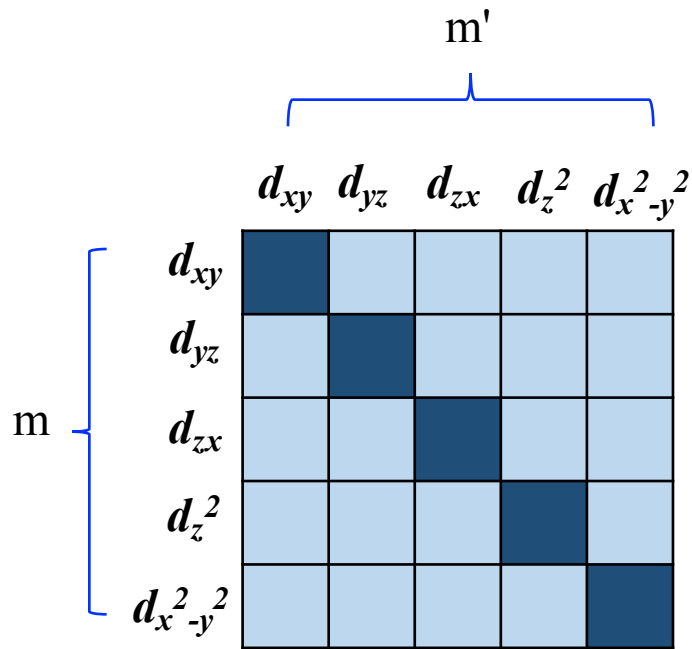
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$\mathbf{n}_{nl}^{I,\sigma}$: occupation matrix of localized states in the nl orbital, atom I , spin index σ

	d_{xy}	d_{yz}	d_{zx}	d_z^2	$d_{x^2-y^2}$
d_{xy}					
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$$n_{mm'}^{I,\sigma} = \sum_{\mathbf{k},v} f_{\mathbf{k},v}^{\sigma} \langle \psi_{\mathbf{k},v} | \phi_{m'}^I \rangle \langle \phi_m^I | \psi_{\mathbf{k},v} \rangle$$

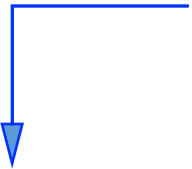
Occupation numbers

$f_{\mathbf{k},v}^{\sigma}$: occupation of KS states
(Fermi-Dirac distribution of ϵ)

DFT + U

$$V_{Total}^{\sigma} = V_{DFT}^{\sigma} + \sum_{I,nl} \sum_m \frac{U_{nl}^I}{2} (1 - 2n_m^{I,\sigma}) |\phi_m^I\rangle \langle \phi_m^I| \quad (11)$$

DFT + U

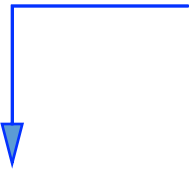


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$n_m^{I,\sigma} < \frac{1}{2} \rightarrow$ Repulsive (+) for less than half-filled orbitals (upward shift)

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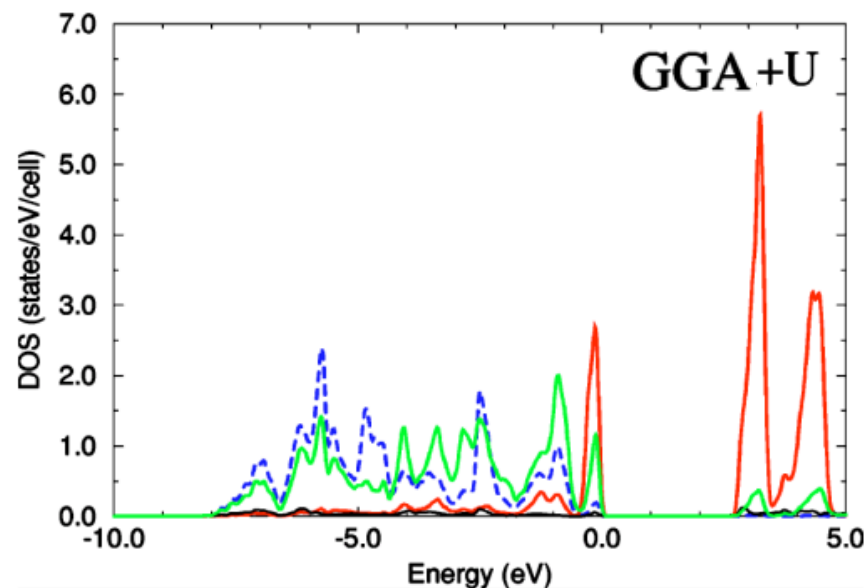
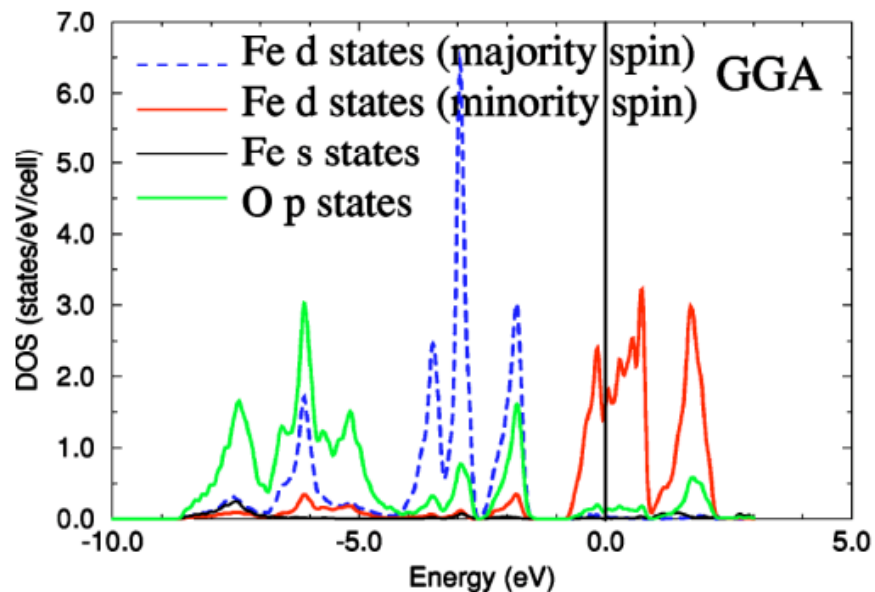
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- DFT+U penalizes fractional occupations by emptying slightly filled orbitals and occupying mostly filled orbitals!

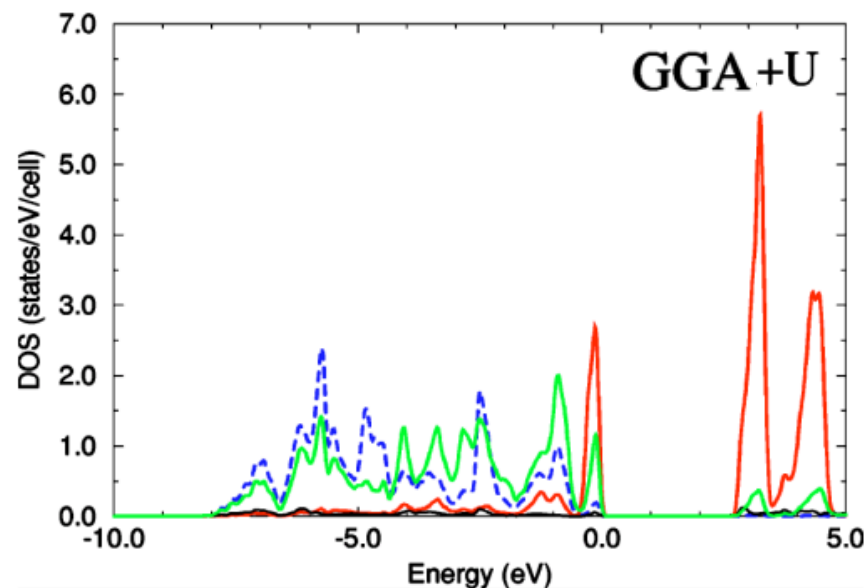
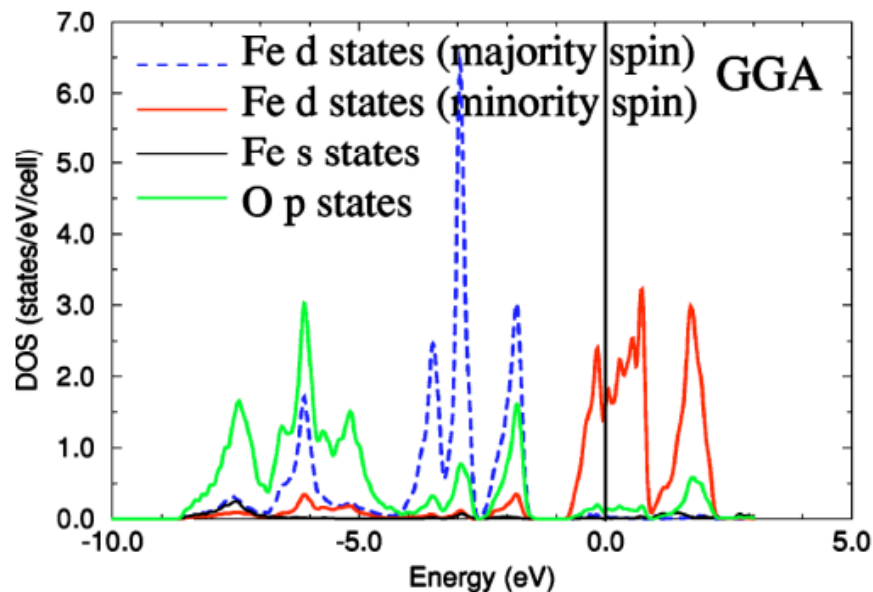
DFT + U

- Hubbard correction:
 - **Discourages** fractional occupations of localized orbitals (often indicating a substantial hybridization with neighbor atoms)
 - **Favors** the Mott localization of electrons on specific atomic states ($n_m^{I,\sigma} \rightarrow 1$) while penalizing the occupation of others ($n_m^{I,\sigma} \rightarrow 0$)

Applications

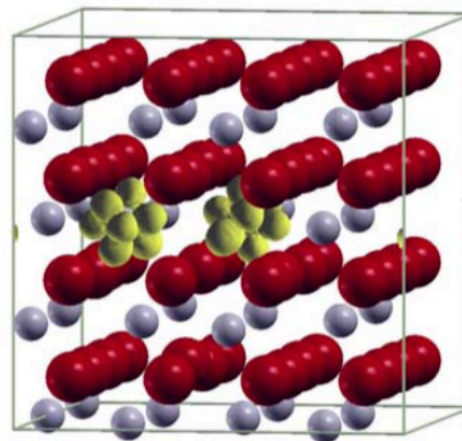
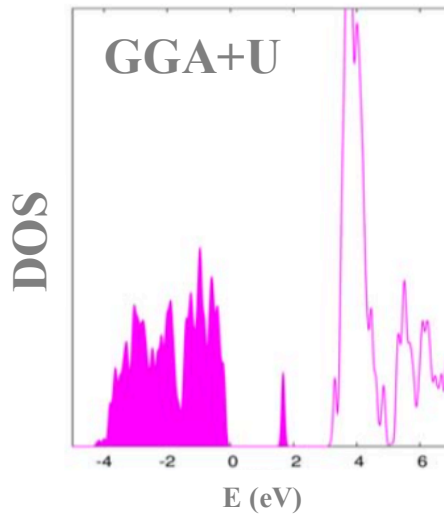
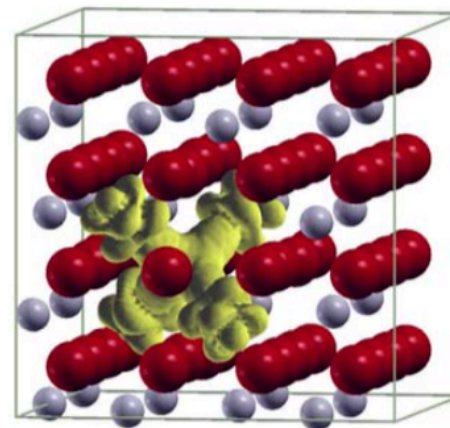
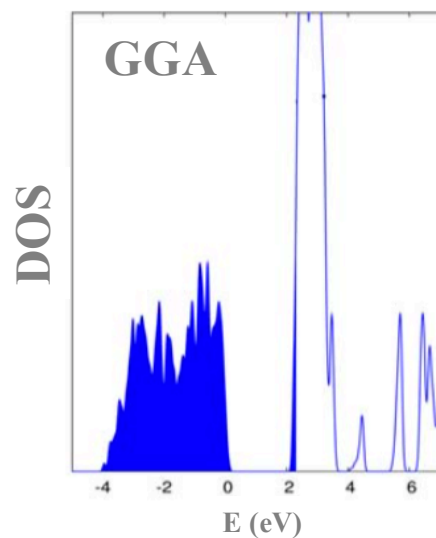
FeO

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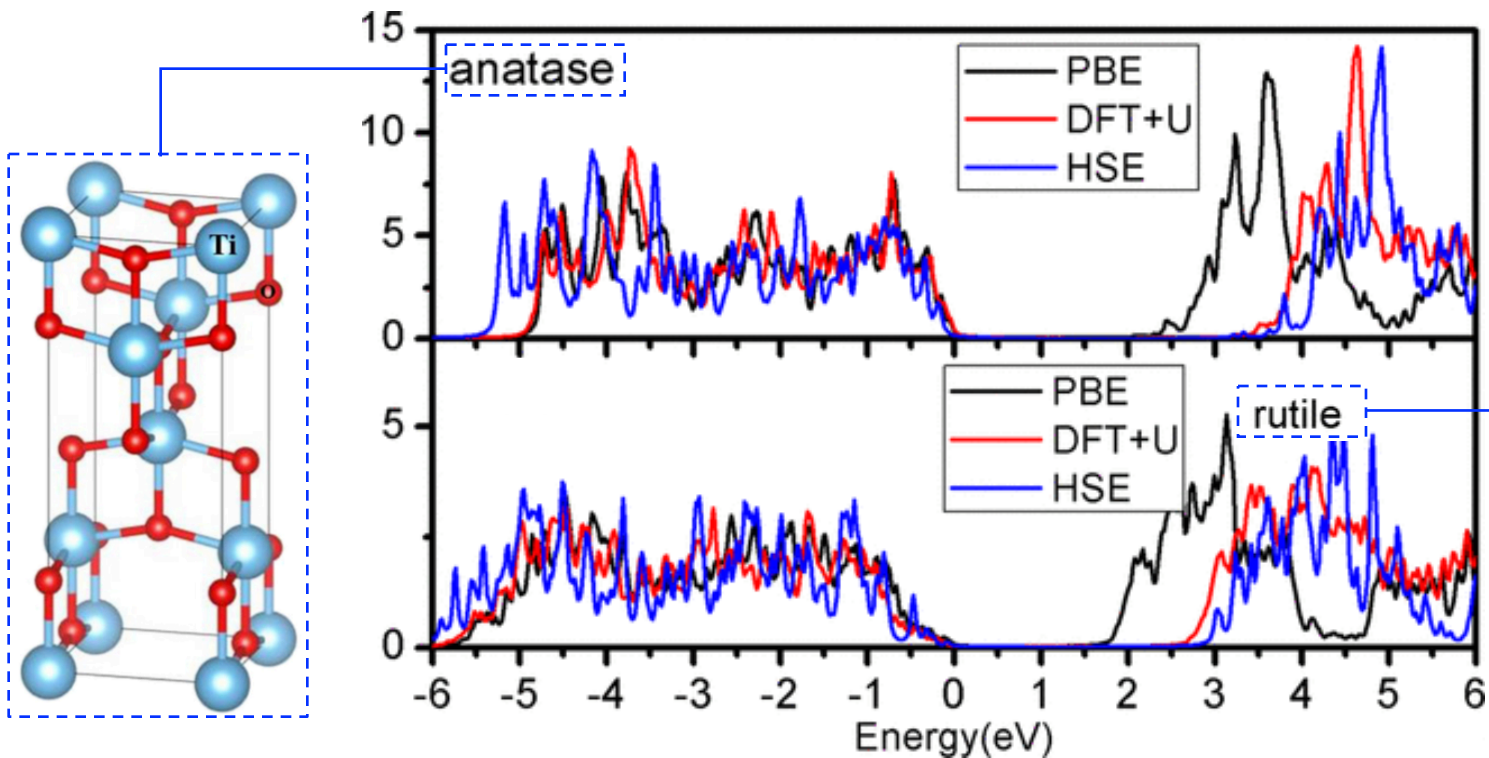
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G. Trimarchi, Z. Wang, and A. Zunger, *Phys. Rev. B* 97, 035107 (2018) $\rightarrow U_{\text{eff}} = 5.0 \text{ eV}$



B. Himmetoglu et al., *Int. J. Quantum Chem.* 114, 14-49 (2014)



Ming-Gang Ju, et al. ACS Appl. Mater. Interfaces 6, 15, 12885–12892 (2014)

Machine learning – DFT+U

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Machine learning the Hubbard U parameter in DFT+ U using Bayesian optimization

Maituo Yu^{1,4}, Shuyang Yang^{1,4}, Chunzhi Wu¹ and Noa Marom^{1,2,3}✉

Within density functional theory (DFT), adding a Hubbard U correction can mitigate some of the deficiencies of local and semi-local exchange-correlation functionals, while maintaining computational efficiency. However, the accuracy of DFT+ U largely depends on the chosen Hubbard U values. We propose an approach to determining the optimal U parameters for a given material by machine learning. The Bayesian optimization (BO) algorithm is used with an objective function formulated to reproduce the band structures produced by more accurate hybrid functionals. This approach is demonstrated for transition metal oxides, europium chalcogenides, and narrow-gap semiconductors. The band structures obtained using the BO U values are in agreement with hybrid functional results. Additionally, comparison to the linear response (LR) approach to determining U demonstrates that the BO method is superior.


npj Computational Materials (2020)6:180; <https://doi.org/10.1038/s41524-020-00446-9>

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-  Correlation? Reminds a self-interaction correction (SIC)
- Hubbard model?
- Calculation of U parameter: Linear-response, DFPT, cRPA, ...
-  Semi-empiricism!

References

- Presentation, text, and references can be found at:

<https://github.com/guirportugal/dft-u-ufabc-2021.git>

THANK YOU!

