Electronic Structure of Perovskites: Lessons from Hybrid Functionals

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Outline

Once Upon a Time in the Ural Mountains

In 1839, the Prussian mineralogist Gustav Rose discovered a new mineral, $CaTiO_3$, which he named perovskite, in honor of the Russian mineralogist Count Lev A. Perovski.

Gustav Rose

$CaTiO_3$

Lev A. Perovski

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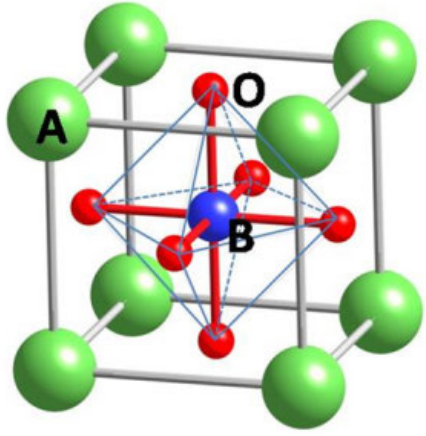
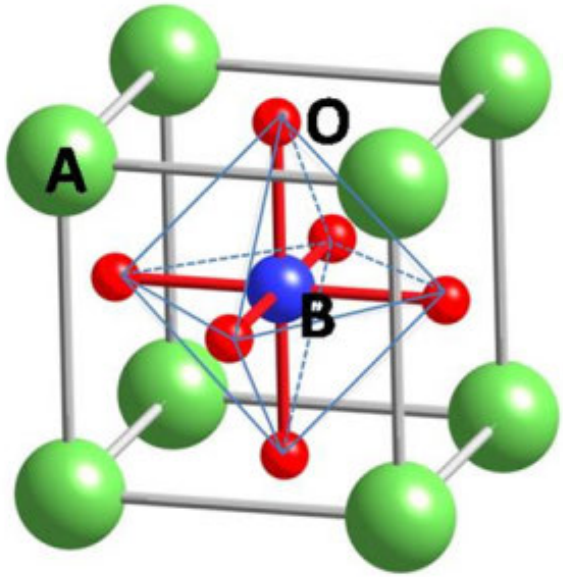


ABO_3

Lev A. Perovski

Basics: Chemistry

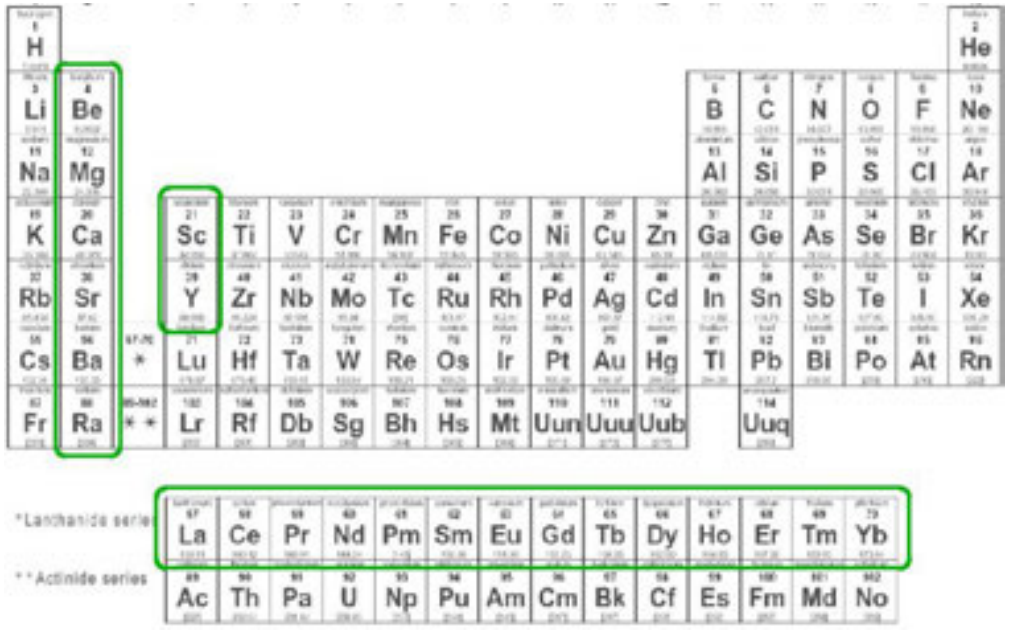


- $A^{2+}B^{4+}O_3^{2-}$: high chemical flexibility

  A-site ion: large cation
  Alkaline earth metal → Ca, Sr, Ba
  Rare earth element → La, Sc, Y

  B-site ion: transition metal (TM) elements
  $3d$ → Ti, V, Mn, Fe, Co, Ni, Cu
  $4d$ → Nb, Tc, Ru, Rh
  $5d$ → Os, Ir

  C-site ion: Oxygen



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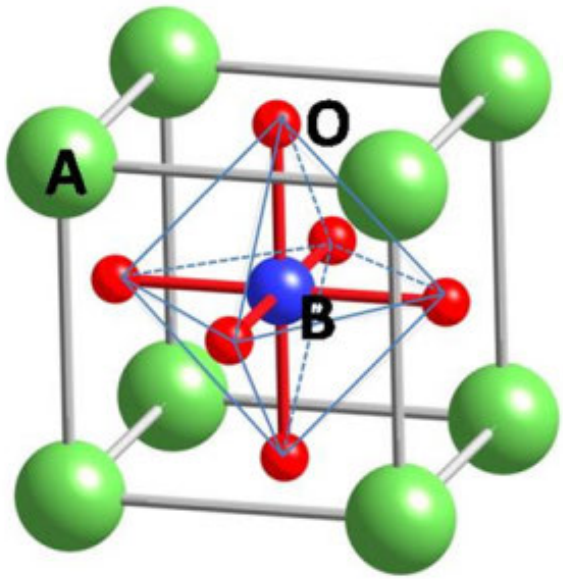

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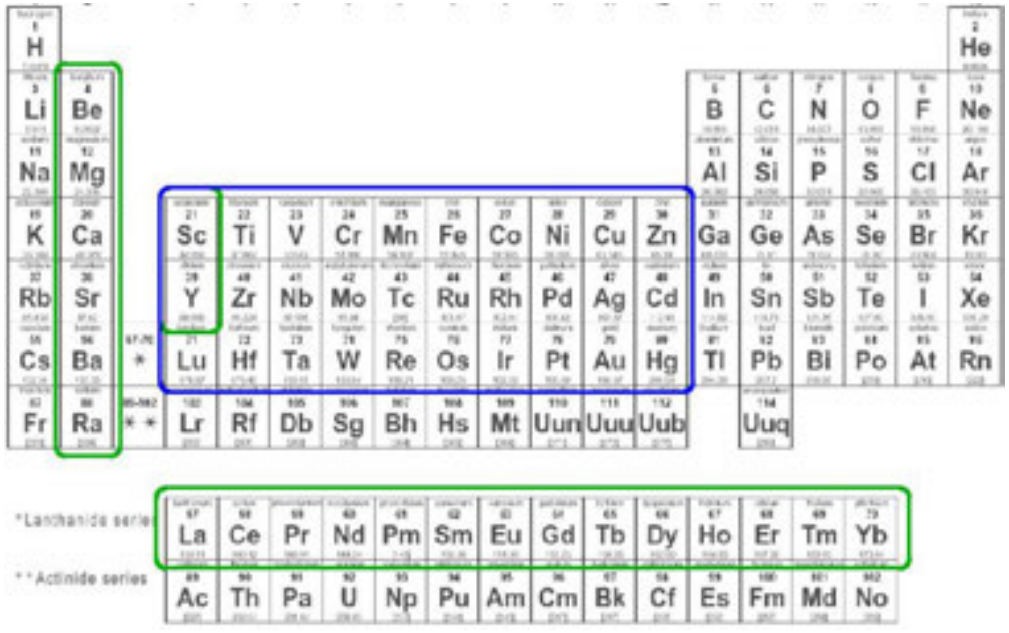

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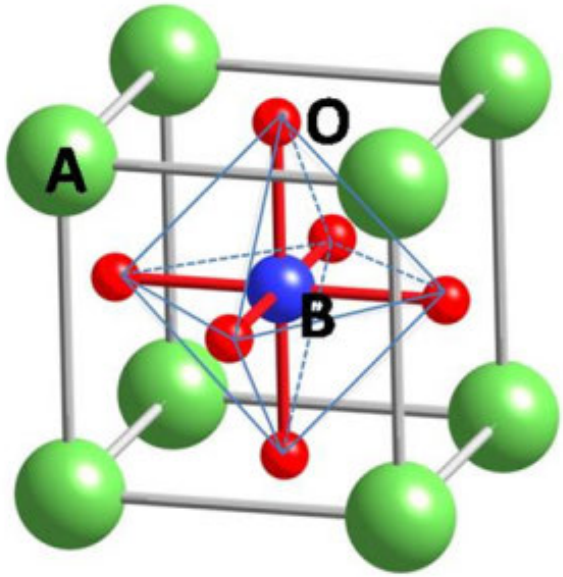

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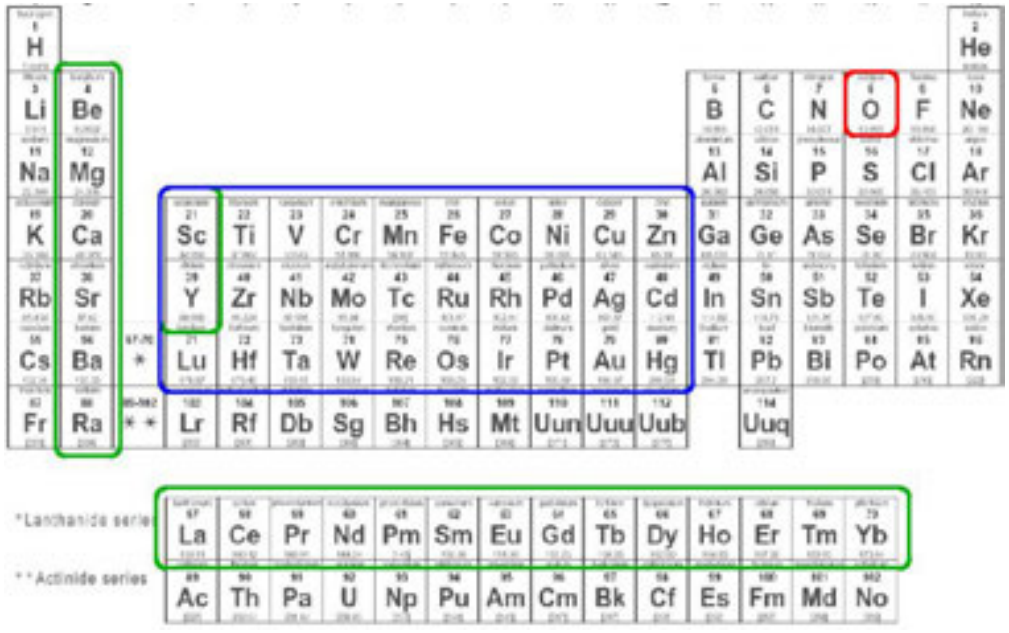
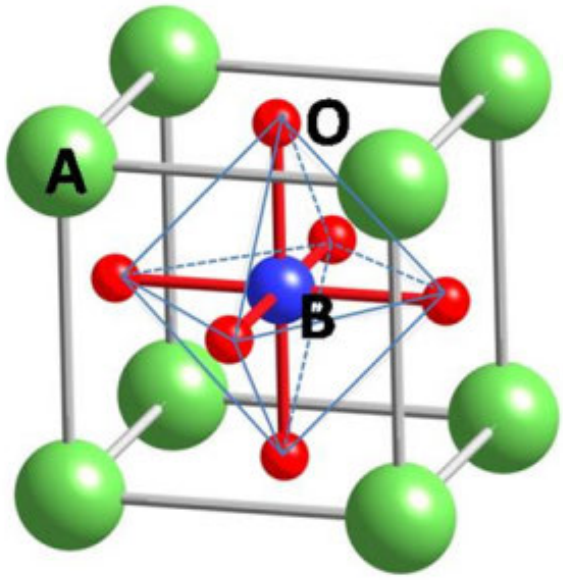


Basics: Structure

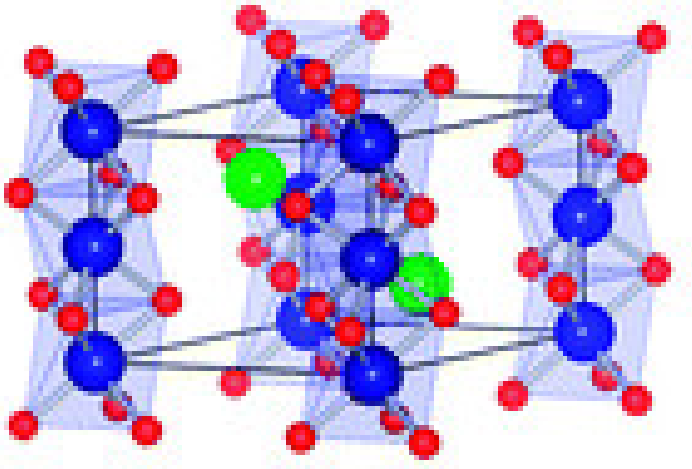


- Goldschmidt tolerance factor t

$$t = (R_A + R_O)/\sqrt{2}(R_B + R_O)$$

t=1	Cubic $(R_A = R_B)$
	$SrTiO_3$
$t > 1$	Hexagonal $(R_A > R_B)$
	face-sharing of octahedra
$t = 0.71 - 0.9$	Orthorhombic $(R_A < R_B)$
	Rhombohedral
$t > 0.71$	Different structures $(R_A \sim R_B)$

Basics: Structure



Fuks *et al.*, J. Mater. Chem. A 1 14320 (2013)

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	$(Ba,Sr)(Co,Fe)O_3$, $BaNiO_3$
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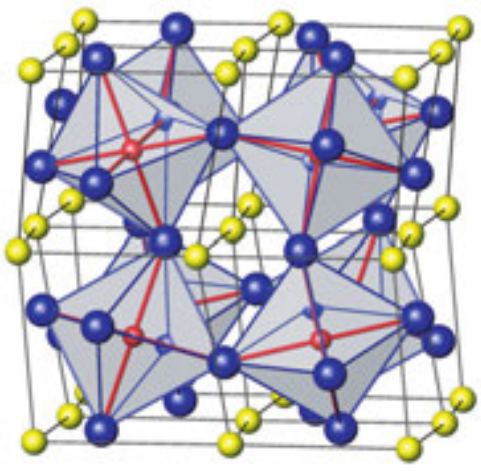

Pavarini *et al.*, New J. Phys. 7, 188 (2005)

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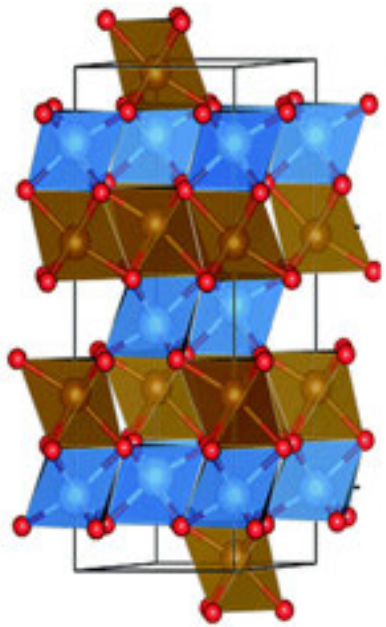

Riberio *et al.*, RSC Adv., 4, 59839 (2014)

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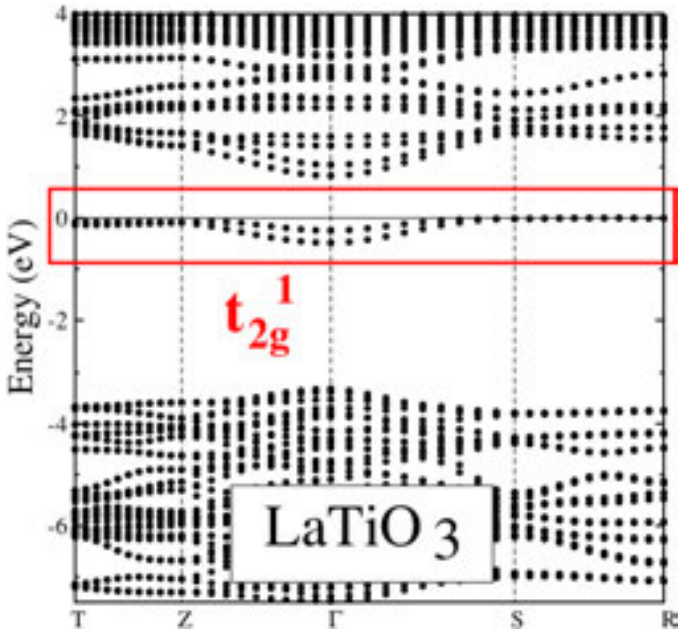
	$FeTiO_3$

Basics: TM electron shell



- Electrons: partially filled (3)d states

  Electron localization (narrow bands, W)
  Strong Coulomb correlations (U)
  U/W $\rightarrow$ Mott–Hubbard insulator

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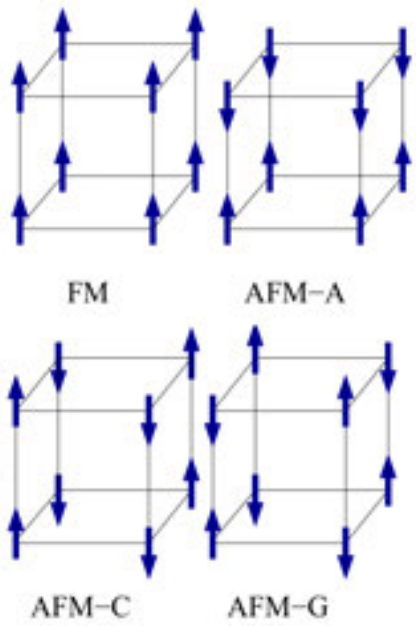

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  Different types of magnetic orderings

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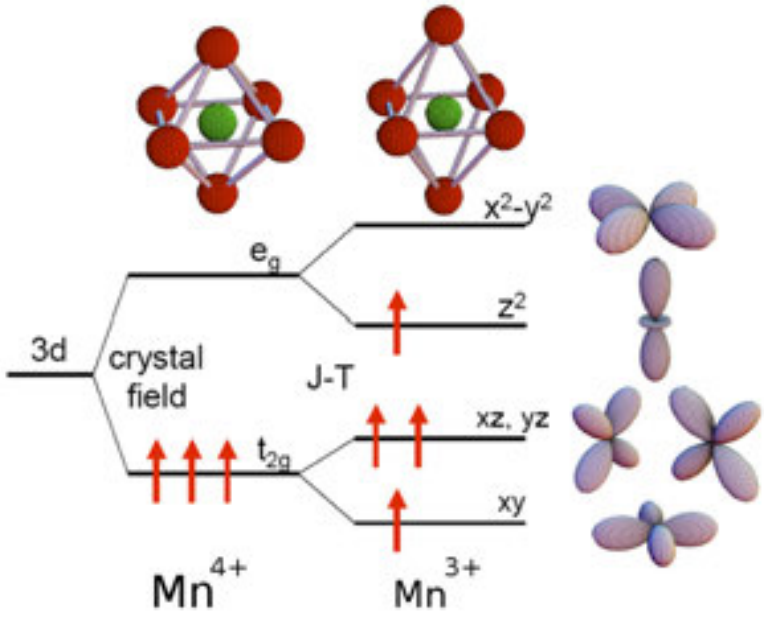

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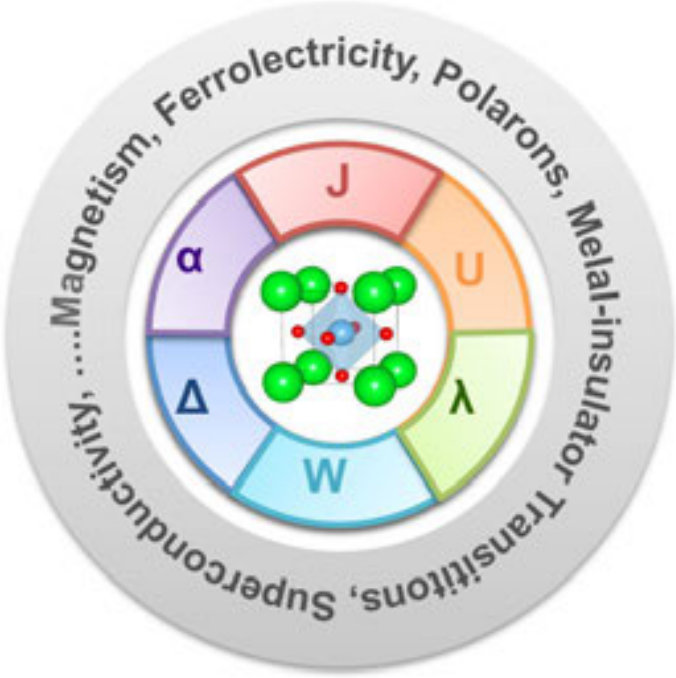
  Jahn-Teller distortions in e_g band perovskites (electron-phonon interaction)

Basics: Many (tunable) competing interactions



W Bandwidth

Δ Crystal Field

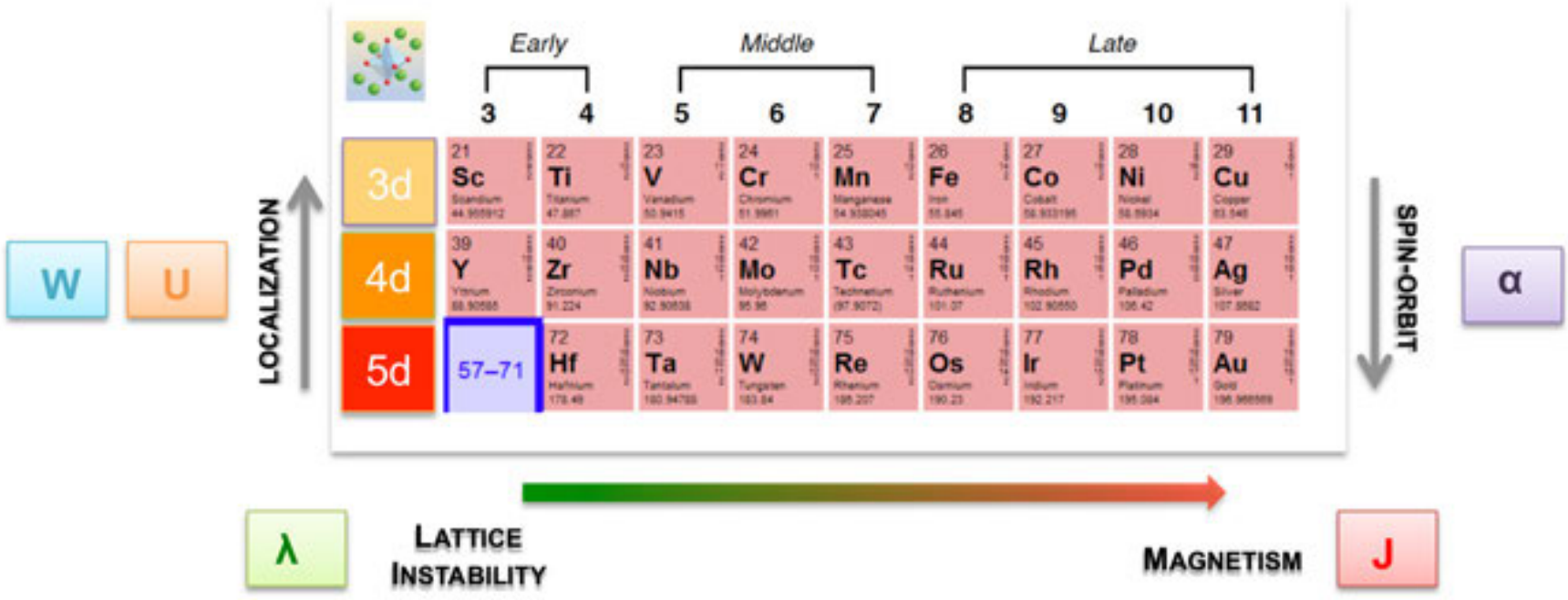
α Spin-orbit

J Hund's coupling

U *e-e* repulsion

λ *e-ph* interaction

Basics: Many (tunable) competing interactions



Competing and tunable energy scales give rise to a variety of functionalities

Basics: Applications

Wide spectrum of attractive properties ⇒ large variety of functional behavior...

Property	Application	Material
Proton conductivity	SOFC electrolyte	
	Hydrogen sensor	$BaCeO_3$, $SrCeO_3$ $BaZrO_3$
	H_2 production/ extraction	
Ionic conductivity	Solid electrolyte	$(La,Sr)(Ga,Mg)O_{3-\delta}$
Mixed conductivity	SOFC electrode	$La(Sr,Ca)MnO_{3-\delta}$, $LaCoO_3$ $(La,Sr)(Co,Fe)O_{3-\delta}$
Ferroelectric/ piezoelectric	Piezoelectric transducer	$BaTiO_3$, $Pb(Zr,Ti)O_3$ $Pb(Mg,Nb)O_3$
	Thermistor, actuator	

Catalytic	Catalyst	$LaFeO_3$, $La(Ce,Co)O_3$
Electrical/ dielectric	Multilayer capacitor	$BaTiO_3$, $BaZrO_3$
	Dielectric ressonator	
	Thin film resistor	
Magnetic	Magnetic memory	$GdFeO_3$, $LaMnO_3$
	Ferromagnetism	
Optical	Electrooptical modulator	$(Pb,La)(Zr,Ti)O_3$
	Laser	$YAlO_3$, $KNbO_3$
Super-conductivity	Superconductor	$Ba(Pb,Bi)O_3$, $BaKBiO_3$

E.C.C. de Souza & R. Muccillo, Materials Research **13** 385 (2010)

Basics: Applications

...and new emerging phenomena

- Oxide electronics: Two dimensional electron gas @ perovskite interface ($SrTiO_3 \| LaAlO_3$) and surface ($SrTiO_3$)
- Spintronics: half-metallic double perovskites
- Photovoltaics: Perovskite solar cells (Halide perovskites, $CH_3NH_3PbX_3$)

Computational Modeling

Realistic modeling of perovskites very challenging: the state of each electron strongly depends on the state of the other electrons of the system, which are coupled (or correlate with each other) via the Coulomb interaction.

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At the core of the problem there is the solution of the many body Hamiltonian.

Basic Hamiltonian of a system of N electrons and M nuclei

$$\begin{aligned}\hat{H} \quad = \quad & -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 - \sum_{n=1}^{M}\frac{\hbar^2}{2M_n}\nabla_n^2 + \frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{i,j=1;i\neq j}^{N}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|} \\ & -\frac{1}{4\pi\epsilon_0}\sum_{n}^{M}\sum_{i}^{N}\frac{Z_n e^2}{|\mathbf{r}_i-\mathbf{R}_n|} + \frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{n,m=1;n\neq m}^{M}\frac{Z_n Z_m e^2}{|\mathbf{R}_n-\mathbf{R}_m|}\end{aligned}$$

The Many Body Hamiltonian

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with

$$\hat{H} = \hat{T}_e$$

The kinetic energy operators for each electron in the system

The Many Body Hamiltonian

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$$\hat{H} = \hat{T}_e + \hat{T}_n$$

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$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{U}_{ee}$$

The potential energy arising from Coulombic electron-electron repulsions

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The potential energy between the electrons and nuclei - the total electron-nucleus Coulombic attraction in the system

The Many Body Hamiltonian

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with

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{U}_{ee} + \hat{U}_{en} + \hat{U}_{nn}$$

The potential energy arising from Coulombic nuclei-nuclei repulsions

One Hamiltonian two communities

First principles (*Ab inito*)

Solution of the many body Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

- No empirical assumptions
- No fitting parameters*
- Full electronic structure**
- Different level of accuracy (approximations)
- Atomistic interpretation

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Model Hamiltonian

Solution of simplified lattice fermion models (typically the Hubbard model)

$$H = -t \sum_{\langle i,j \rangle, \sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + c^{\dagger}_{j,\sigma} c_{i,\sigma}) + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow}$$

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- Short-ranged electron interactions
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- Accurate solution, transparent physical interpretation

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FP+MH $\rightarrow DFT(GW) + DMFT$

Anisimov *et al.*, J. Phys. Condensed Matter **35**, 7359 (1997)

K. Held, Advances in Physics **56**, 829 (2007)

Approximations

$$\hat{H}\Psi = E\Psi$$

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$$\hat{H}_e\Psi = E\Psi, \quad \hat{H}_e = T_e + V_{ee} + V_{en}$$

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Many-body $\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$ storage requirements prohibitive

$$(\#\text{grid points})^N$$

2. Map to "one-electron" theory

Density Functional Theory (LDA, GGA)

$$\&$$

Hartree-Fock (EXX)

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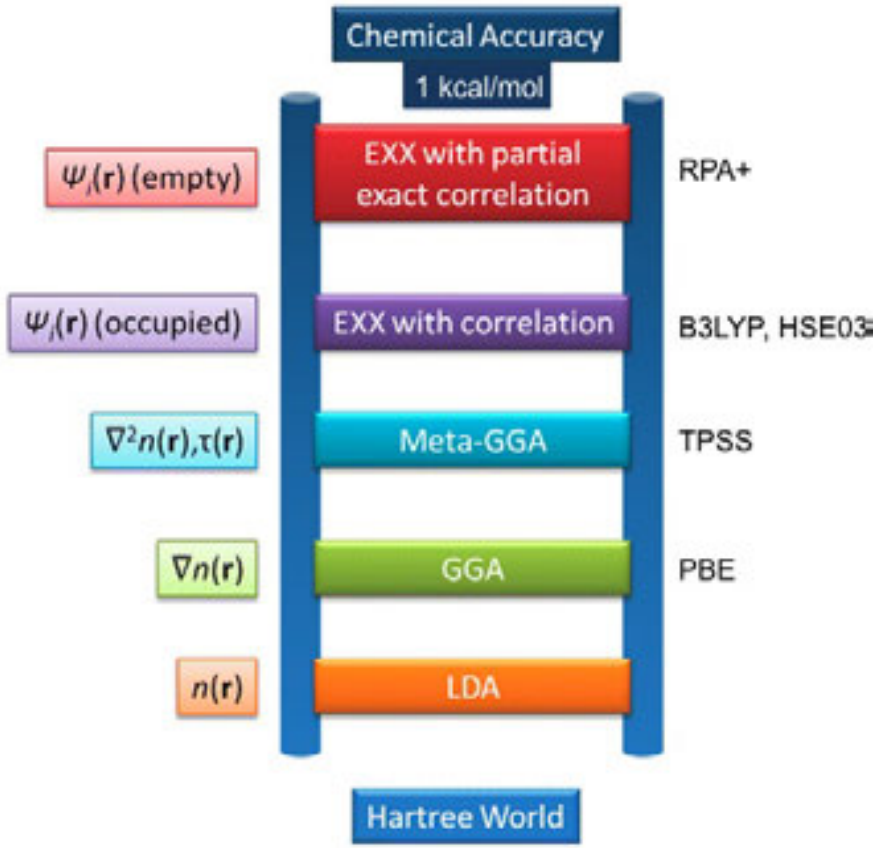
The Jacob ladder



Solution of the full electronic Schrödinger equation

$$\hat{H}_e \Psi = E\Psi$$

Hartree: non-interacting (NI) particles (independent particle approximation)

$$\Psi^{HP}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \quad = \quad \phi_1(\mathbf{x}_1)\,\phi_2(\mathbf{x}_2)\ldots\phi_N(\mathbf{x}_N)$$

where $\phi(\mathbf{x})$ is an eigenstate of:

$$\hat{H}_e^{NI} \quad = \quad -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{4\pi\epsilon_0}\sum_{n}^{M}\sum_{i}^{N}\frac{Z_n e^2}{|\mathbf{r}_i - \mathbf{R}_n|} = \sum_{i=1}^{N} h(\mathbf{r}_i)$$

Variational principle:

$$\langle H_e \rangle \equiv \frac{\langle \Psi^{HP}|\hat{H}_e|\Psi^{HP}\rangle}{\langle \Psi^{HP}|\Psi^{HP}\rangle} \geqslant E_0$$

The Hartree World:

$$\Psi^{HP}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \phi_1(\mathbf{x}_1)\,\phi_2(\mathbf{x}_2)\ldots\phi_N(\mathbf{x}_N)$$

Limitation of the Hartree product:

1. *Uncorrelated* probability distribution:

$$\rho(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = |\phi_1(\mathbf{x}_1)|^2 |\phi_2(\mathbf{x}_2)|^2 \ldots |\phi_N(\mathbf{x}_N)|^2$$

The interaction among particles taken into account through the Hartree term, i.e. electrostatic potential arising from the charge distribution of N electrons:

$$\sum_{i=1}^{N} \int dx' |\phi_i(\mathbf{x}')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

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2. *Self interaction error*:

   The Hartree-term includes a sum over all electrons

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1. *Uncorrelated* probability distribution:

$$\rho(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = |\phi_1(\mathbf{x}_1)|^2 |\phi_2(\mathbf{x}_2)|^2 \ldots |\phi_N(\mathbf{x}_N)|^2$$

   The interaction among particles taken into account through the Hartree term, i.e. electrostatic potential arising from the charge distribution of N electrons:

$$\sum_{i=1}^{N} \int dx' |\phi_i(\mathbf{x}')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

2. *Self interaction error*:

   The Hartree-term includes a sum over all electrons

3. Ψ^{HP} is *not Antisymmetric*

$$\mathscr{P}_{1,2}\left[\psi_1(\mathbf{x}_1)\,\psi_2(\mathbf{x}_2)\ldots\psi_N(\mathbf{x}_N)\right] = \psi_1(\mathbf{x}_2)\,\psi_2(\mathbf{x}_1)\ldots\psi_N(\mathbf{x}_N) \neq -\psi_1(\mathbf{x}_1)\,\psi_2(\mathbf{x}_2)\ldots\psi_N(\mathbf{x}_N)$$

In the HF method the WF the WF is written as a Slater determinant.

$$\Psi^{HP}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \phi_1(\mathbf{x}_1)\,\phi_2(\mathbf{x}_2)\ldots\phi_N(\mathbf{x}_N)$$

$$\Downarrow$$

$$\Psi_{\mathrm{AS}}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \ldots & \phi_N(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \ldots & \phi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \phi_1(\mathbf{x}_N) & \phi_2(\mathbf{x}_N) & \ldots & \phi_N(\mathbf{x}_N) \end{vmatrix}$$

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$$\Psi^{HP}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \phi_1(\mathbf{x}_1)\,\phi_2(\mathbf{x}_2)\ldots\phi_N(\mathbf{x}_N)$$

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1. *Antisymmetric*
2. *Self interaction free*
3. *Uncorrelated*

   Only particles with the same spin have a certain degree of correlation:

   $$\rho(\mathbf{x}_1, \mathbf{x}_2) = 0 \quad \text{if} \quad \mathbf{r}_1 = \mathbf{r}_2$$

   Pauli principle

The Hartree-Fock equations:

1. Electronic Hamiltonian $\hat{H}_e = T_e + V_{ee} + V_{en}$

$$\hat{H}_e = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \frac{1}{2}\sum_{i,j=1;i\neq j}^{N}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|} - \sum_n^M\sum_i^N\frac{Z_n e^2}{|\mathbf{r}_i-\mathbf{R}_n|}$$

2. WF $\rightarrow$ Slater determinant Ψ_{AS}
3. $\langle\Psi_{\mathrm{AS}}|\hat{H}_e|\Psi_{\mathrm{AS}}\rangle$
4. Variation principle

$$\Downarrow$$

$$\left[-\frac{1}{2}\nabla^2 - \sum_n\frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|}\right]\psi_k(\mathbf{x}) + \sum_{l=1}^{N}\int dx'|\psi_l(\mathbf{x}')|^2\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_k(\mathbf{x})$$

$$-\sum_{l=1}^{N}\int dx'\psi_l^*(\mathbf{x}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_k(\mathbf{x}')\psi_l(\mathbf{x}) = \epsilon_k\psi_k$$

It has the form of a Schrödinger equation, where the eigenvalues ϵ_k represent the orbital energies. One more term: EXCHANGE.

$$\hat{\mathscr{F}}\psi_k = \left[-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|}\right]\psi_k(\mathbf{x}) + \sum_{l=1}^{N}\int dx' |\psi_l(\mathbf{x}')|^2 \frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_k(\mathbf{x})$$

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1. Hartree term only: unphysical coupling between orbital k and itself (self-energy)
2. Exchange term non-local: its value at $\mathbf{r}$ depends on $\psi_k(\mathbf{r}')$

   The Exchange term is the same as the Hartree term, with two spin-orbitals labels k and l interchanged and a *minus* sign.
3. Fock+Hartree: self-energy problem solved

The Fock operator $\hat{\mathscr{F}}$ is a one particle operator. It replaces the many-body Schrödinger equation by a set of one-particle equations, in which each electron moves in an effective field, often also called *mean-field*.

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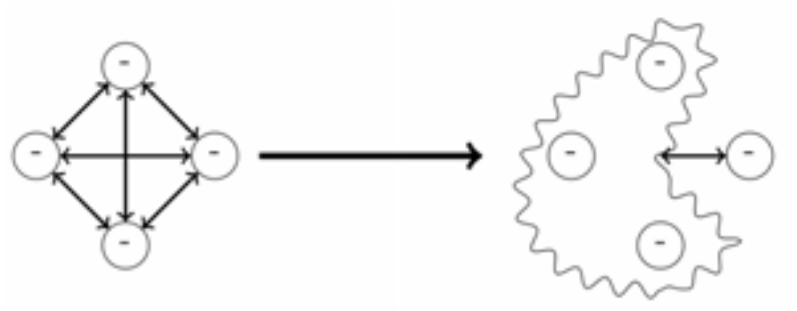

Many-body problem $\longrightarrow$ one-electron problems

The WF does not have explicit dependence on the position of all other electrons. The dependence is only implicit via the Exchange term.

Hartree-Fock equations:

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + V_e(\mathbf{r}) + V_H(\mathbf{r})\right)\phi_i(\mathbf{r}) + \int V_x(\mathbf{r},\mathbf{r}')\phi_i(\mathbf{r}')d^3r' = \epsilon_i^{HF}\phi_i(\mathbf{r})$$

- Mean-field
- WF-based method: Slater determinant
- *exact* exchange V_x
- no correlation (only Pauli principle)
- Self-interaction free

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DFT equations:

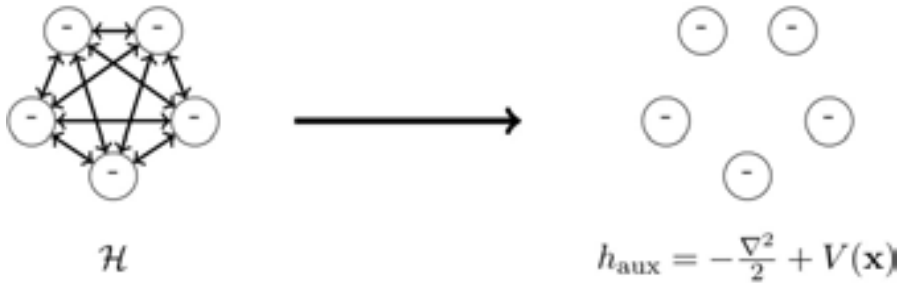
$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + V_{en}(\mathbf{r}) + V_H + V_{xc}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i^{KS}\phi_i(\mathbf{r})$$

1. Mean-field
2. Density-based method
3. *approximate* exchange & correlation, V_{xc}
4. Self-interaction problem

Density Functional Theory

1. Mean-field

   The real interacting system is replaced by an effective Kohn-Sham (KS) system of non-interacting electrons in an effective potential V.



$$H \rightarrow \sum_{i=1}^{N} h_{aux}; \qquad h_{aux}\phi_i = \epsilon_i \phi_i; \qquad \phi_i = \text{KS single} - \text{particle orbitals}$$

2. Density-based method

   The DFT approach promotes the particle density

$$n(\mathbf{r}) = \sum_{i,\text{occupied}} |\phi_i(\mathbf{r})|^2.$$

   to the status of key variable, on which the calculation of all other observables can be based (Hohenberg-Kohn Theorem)

$$\begin{array}{ccc} \mathsf{V}_{ext}(\mathbf{r}) & \overset{HK}{\Leftarrow} & \mathsf{n}_0(\mathbf{r}) \\ \Downarrow & & \Uparrow \\ \Psi_i(\mathbf{r}) & \Rightarrow & \Psi_0(\mathbf{r}) \end{array}$$

3. *approximate* exchange and correlation, V_{xc}
   Universal functional for the energy given in terms of the density:

$$E[n] = T_{KS}[n] + \int d^3 n(\mathbf{r}) V_{ext}(\mathbf{r}) + \frac{e^2}{2} \int\int d^3 r d^3 r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n]$$

$$E[n] \geqslant E[n_{GS}] = E_{GS}^{True}$$

The quality of the solution depend on the (*unknown*) form of the XC potential V_{xc}:

$$V_{xc}([n], \mathbf{r}) = \frac{\delta E_{XC}}{\delta n(\mathbf{r})}$$

Approximations needed:

$$E_{xc}^{LDA}[n] = \int dr^3 e_{xc}(n(\mathbf{r}))$$

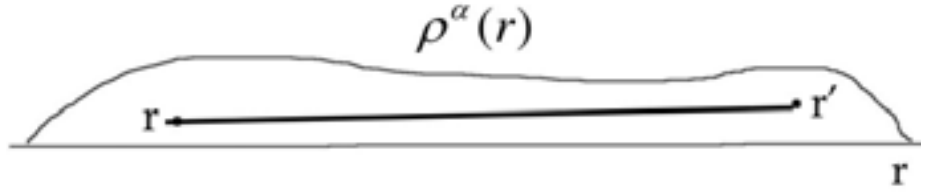
$$E_{xc}^{GGA}[n] = \int dr^3 f(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

4. Self-interaction problem

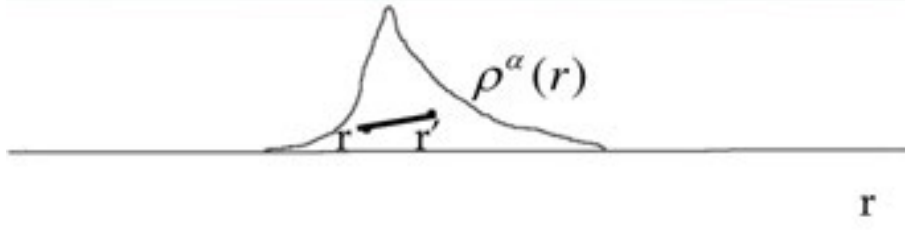
   Non complete cancellation of the spurious repulsion of each electron from itself, included in the Hartree term, that is not completely accounted for in XC functionals:

$$\Delta\epsilon = \int\int \frac{n_1(\mathbf{r})n_1(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

Delocalized States $\rightarrow$ small Errors



Localized States $\rightarrow$ large Errors



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- WF-based method: Slater determinant
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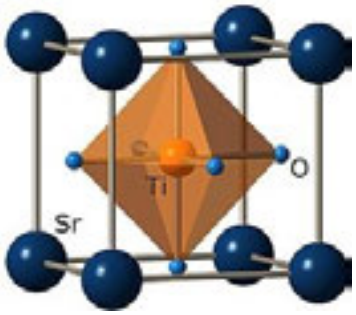
Hands-on: DFT & HF (VASP)

Test case: $SrTiO_3$



	DFT(GGA)	HF	Expt.
Direct gap (eV) $\Gamma - \Gamma$	?	?	3.75
Running time	?	?	

Hands-on: DFT & HF (VASP)

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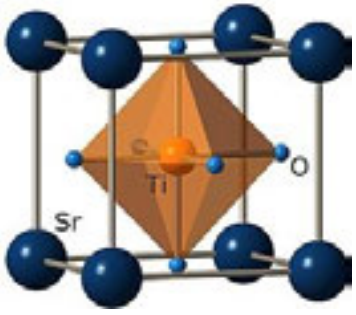

	DFT(GGA)	HF	Expt.
Direct gap (eV) $(\Gamma - \Gamma)$	2.16	4.66	3.75
CPU time (s)	5	613	

Hands-on: DFT & HF (VASP)

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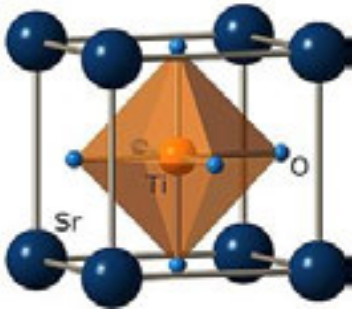

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Direct gap (eV) $(\Gamma - \Gamma)$	2.16	4.66	3.75
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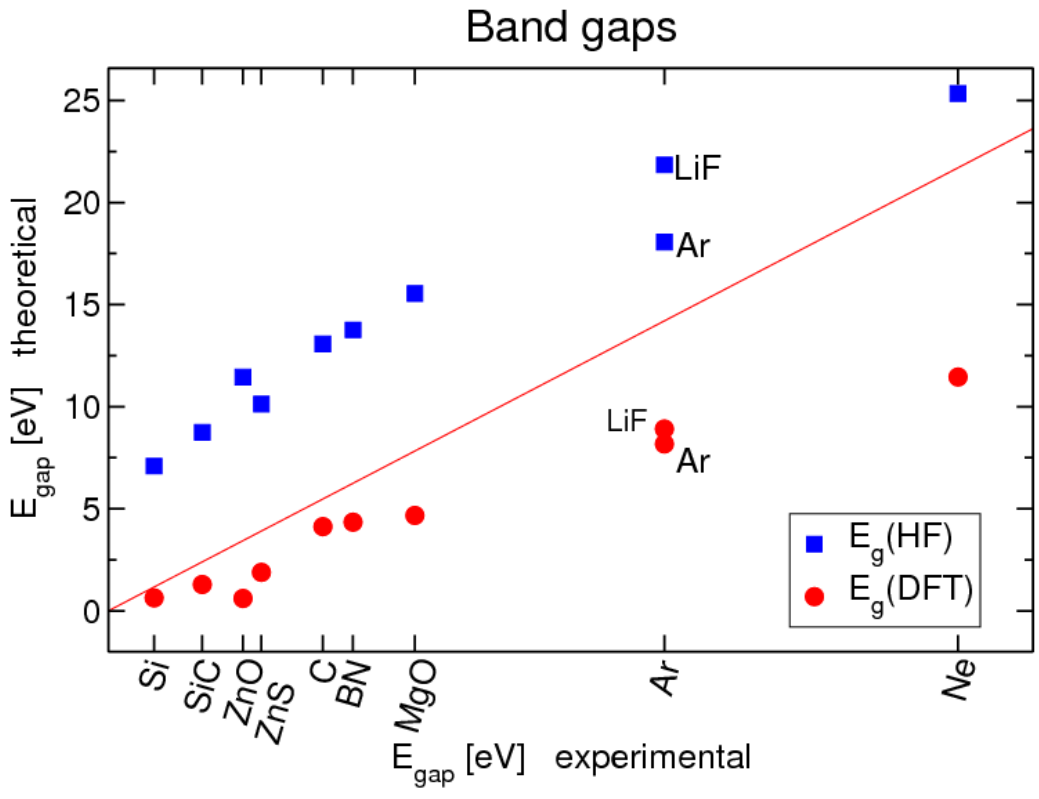
DFT

1. band gap too small
   (self-interaction problem)
2. fast
   (approx. E_{xc})

HF

1. band gap too large
   (no correlation)
2. slow
   (two-particle integral, exact exchange)

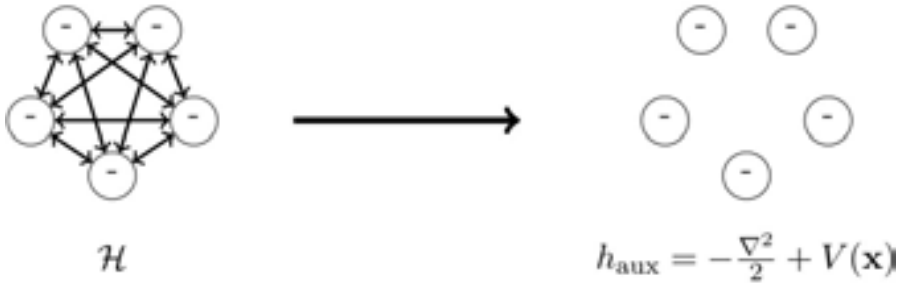
DFT vs. HF



General trend: DFT tends to underestimate band gaps, HF overestimates

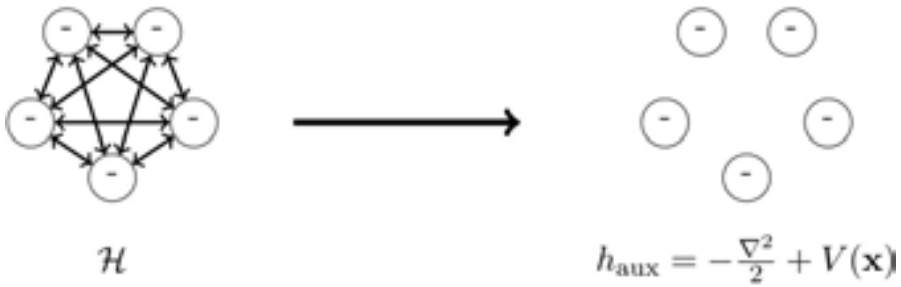
DFT + HF ?

Adiabatic connection and coupling-constant integration



The adiabatic connection continuously transform the real interacting system to the non-interacting one

Adiabatic connection and coupling-constant integration



The adiabatic connection continuously transform the real interacting system to the non-interacting one

$$V_{ee} \rightarrow \lambda V_{ee} \qquad \text{with} \qquad 0 \leqslant \lambda \leqslant 1$$

$\lambda = 0$: non-interacting KS system $\rightarrow \Psi_{\lambda=0}=$ KS-WF

$\lambda = 1$: exact many-body systems $\rightarrow \Psi_{\lambda=1}=$ Exact many-body WF

$$E_{XC} = \int_0^1 E_{xc,\lambda} d\lambda, \qquad E_{xc,\lambda} = \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle - E_H$$

Adiabatic connection and coupling-constant integration

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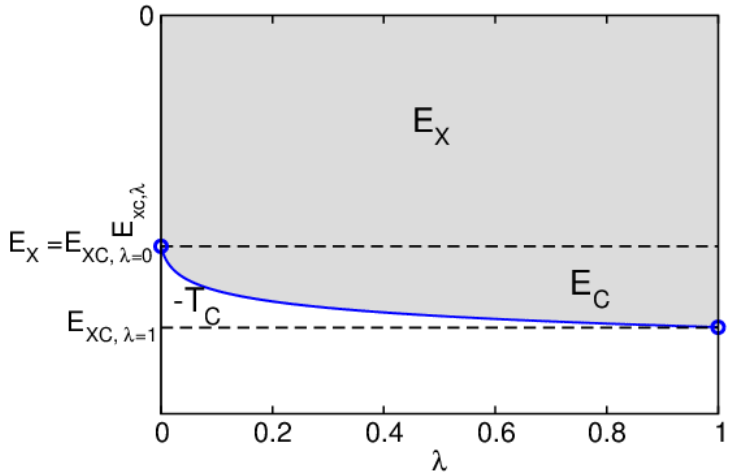
$E_{xc,\lambda}$ is a monotonically decreasing function of λ



The area between the curve and the x-axis is just E_{xc}.

Adiabatic connection and coupling-constant integration

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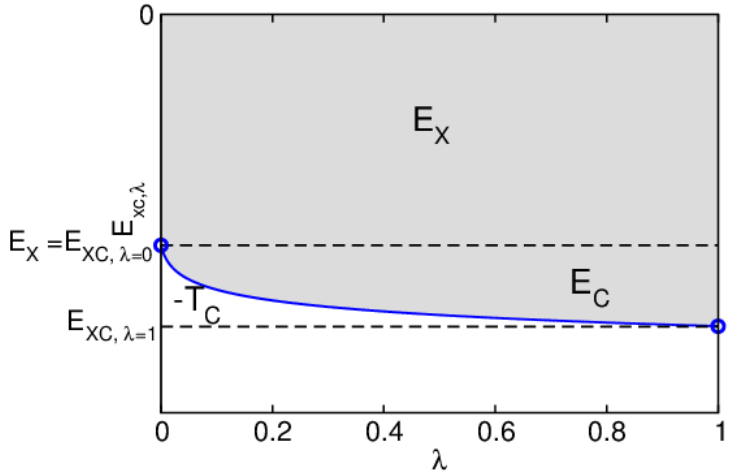

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The integral can be approximated via linear interpolation:

$$E_{XC} \approx \frac{1}{2} E_{XC,\lambda=0} + \frac{1}{2} E_{XC,\lambda=1}$$

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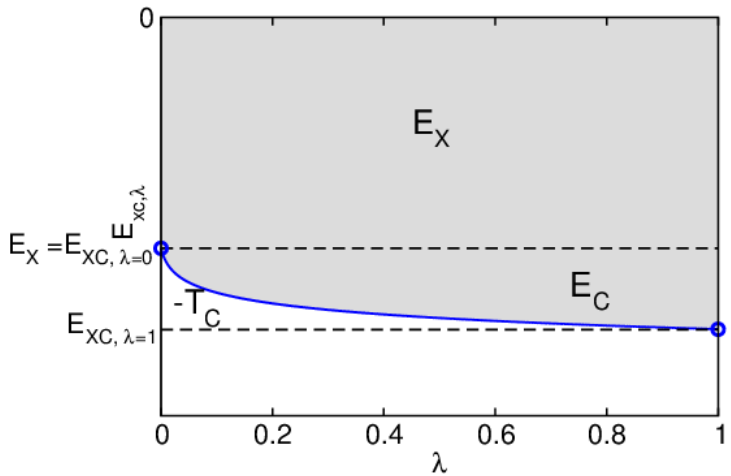

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A.D. Becke, J. Chem. Phys. **98**, 1372 (1993)

The Hybrid Functionals Family

Half-Half, Becke 1993

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B3LYP, Becke 1993-1994

$$E_{XC}^{\text{B3LYP}} = E_X^{LDA} + \alpha_1(E_X^{HF} - E_X^{LDA}) + \alpha_2(E_X^{GGA} - E_X^{LDA}) + \alpha_3(E_C^{GGA} - E_C^{LDA})$$

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PBE0, Perdew-Burke-Ernzerhof 1996

$$E_{XC}^{\text{PBE0}} = E_C^{PBE} + \alpha E_X^{HF} + (1-\alpha)E_X^{PBE},$$

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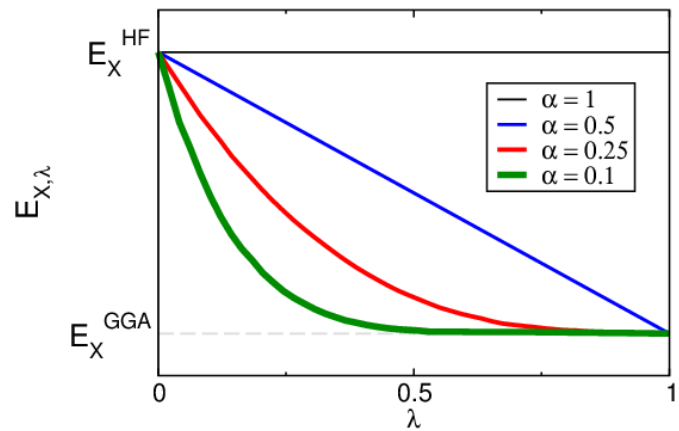
$$E_{XC}^{\text{PBE0}} = E_C^{PBE} + \alpha E_X^{HF} + (1-\alpha)E_X^{PBE},$$

Choice of α

Optimum: $\alpha = 0.25$ (fit to MP2) →

In practice α is system dependent



Disadvantages

Long-range E_X numerically complicated

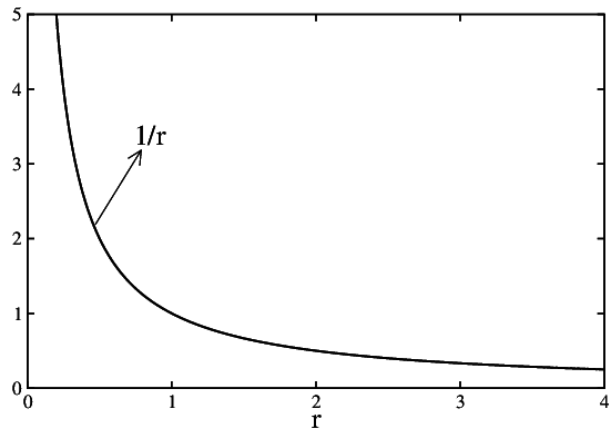
Screened Hybrid Functionals: HSE

From PBE0 to HSE

$$V_x \rightarrow V_{sx}$$

$$-e^2 \frac{\sum_j f_j \phi_j(\mathbf{r}) \phi_j{}^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad \rightarrow \quad -e^2 \sum_j f_j \phi_j(\mathbf{r}) \phi_j{}^*(\mathbf{r}') \frac{\mathrm{erfc}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}$$

$$\frac{1}{r} = \underbrace{\frac{\mathrm{erfc}(\mu r)}{r}}_{\text{sr}} + \underbrace{\frac{\mathrm{erf}(\mu r)}{r}}_{\text{lr}}$$



$$E_{XC}^{\mathrm{HSE}} = \alpha E_X^{HF,sr}(\mu) + (1-\alpha) E_X^{PBE,sr}(\mu) + \alpha E_X^{PBE,lr}(\mu) + E_C^{PBE}$$

Default values:

$\alpha = 0.25;$ $\mu = 0.2$ Å^{-1}

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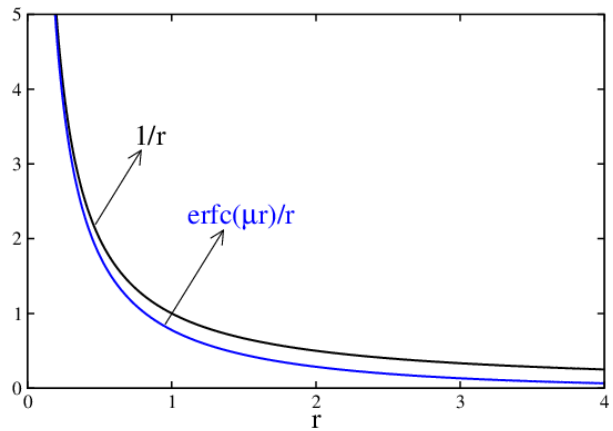

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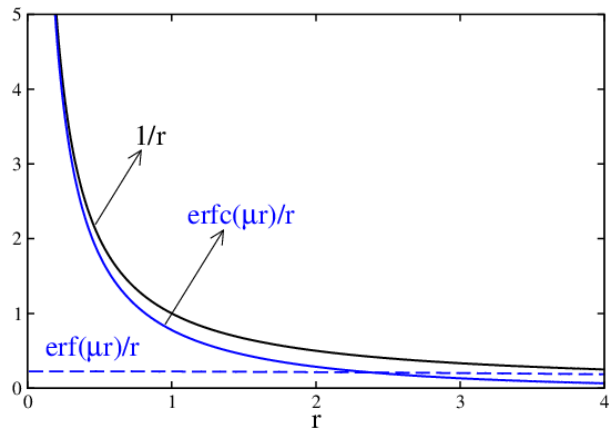

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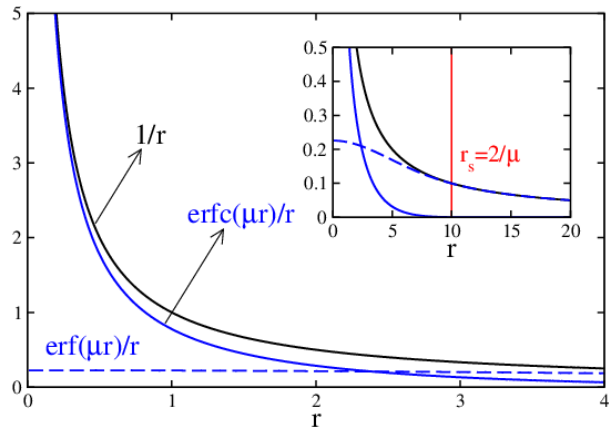
$$-e^2 \frac{\sum_j f_j \phi_j(\mathbf{r}) \phi_j{}^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad \rightarrow \quad -e^2 \sum_j f_j \phi_j(\mathbf{r}) \phi_j{}^*(\mathbf{r}') \frac{\mathrm{erfc}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}$$

$$\frac{1}{r} = \underbrace{\frac{\mathrm{erfc}(\mu r)}{r}}_{\text{sr}} + \underbrace{\frac{\mathrm{erf}(\mu r)}{r}}_{\text{lr}}$$



$$E_{XC}^{\mathrm{HSE}} = \alpha E_X^{HF,sr}(\mu) + (1-\alpha) E_X^{PBE,sr}(\mu) + \alpha E_X^{PBE,lr}(\mu) + E_C^{PBE}$$

Default values:

$\alpha = 0.25;$ $\mu = 0.2$ Å^{-1}

Screened Hybrid Functionals

Why Screening

- Computational convenience: neglect numerically complex long-range part of E_X
- Physical justification: in many-body systems the unscreened exchange is reduced

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Hybrid Functionals meets GW

- DFT

$$\left(-\frac{1}{2}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

- HF

$$\left(-\frac{1}{2}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int V_{\text{X}}(\mathbf{r},\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}' = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

- HSE

$$\left(-\frac{1}{2}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{c}}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int V_{\text{sX}}^{HSE}(\mathbf{r},\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}' = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

- Quasiparticle equations (GW)

$$\left(-\frac{1}{2}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}',E_{n\mathbf{k}})\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}' = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

Hybrid Functionals meets GW

- HSE

$$\left(-\frac{1}{2}\Delta + V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r}) + V_{\rm c}(\mathbf{r}) + \alpha V_{\rm x}^{lr}(\mathbf{r}) + (1-\alpha)V_{\rm x}^{sr}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int \alpha V_{\rm x}^{sr}(\mathbf{r},\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}'$$

- Quasiparticle equations (GW)

$$\left(-\frac{1}{2}\Delta + V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}',E_{n\mathbf{k}})\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}'$$

$$\Sigma(\omega) = iG(\omega)W(\omega)$$

W = screened (GW) Coulomb interaction

$$W(\omega) = \epsilon(\omega)^{-1}v \xrightarrow{\epsilon(\omega)\to\epsilon_\infty = 1/\alpha} \alpha v \xrightarrow{v\to v_{sr}} \alpha\frac{erfc(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}$$

Hybrid Functionals meets GW

- HSE

$$\left(-\frac{1}{2}\Delta + V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r}) + V_{\rm c}(\mathbf{r}) + \alpha V_{\rm x}^{lr}(\mathbf{r}) + (1-\alpha)V_{\rm x}^{sr}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int \alpha V_{\rm x}^{sr}(\mathbf{r},\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}'$$

- Quasiparticle equations (GW)

$$\left(-\frac{1}{2}\Delta + V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}',E_{n\mathbf{k}})\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}'$$

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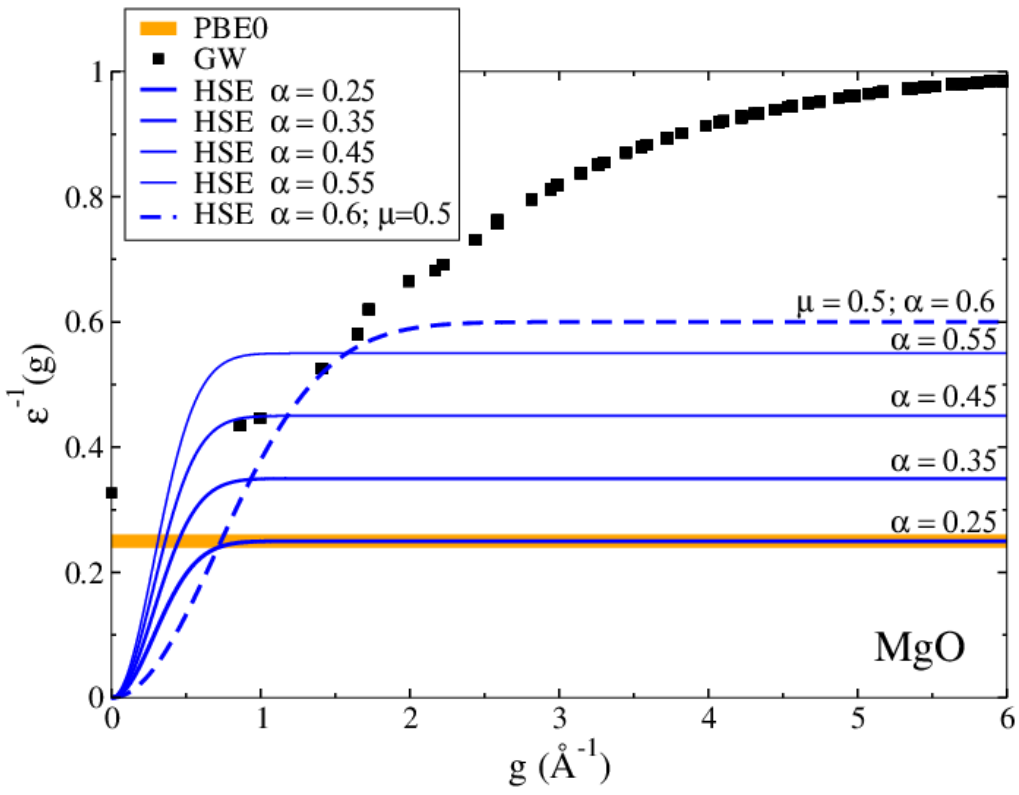
Optimum $\alpha = \frac{1}{\epsilon_\infty}$

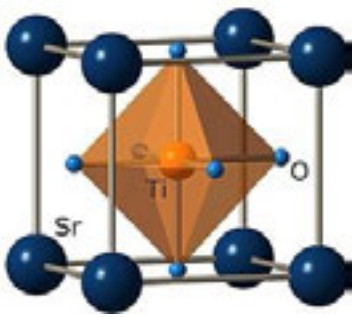
but HSE is NOT GW!



- No Exchange at short wave vector (good only for metals)
- 0.25 choice questionable for wide band gap (small ϵ_∞) materials
  better choice $\alpha = \frac{1}{\epsilon_\infty}$
- α and μ fitting parameters

Hands-on: HSE (VASP)

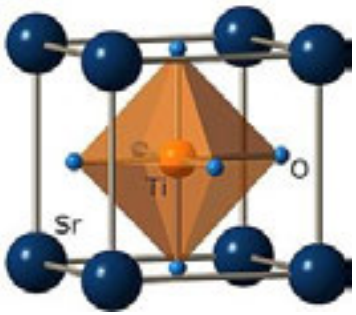
Test case: $SrTiO_3$



	DFT(GGA)	HF	HSE	Expt.
Direct gap (eV) $(\Gamma - \Gamma)$	2.16	4.66	?	3.75
CPU time (s)	5	613	?	

Hands-on: HSE (VASP)

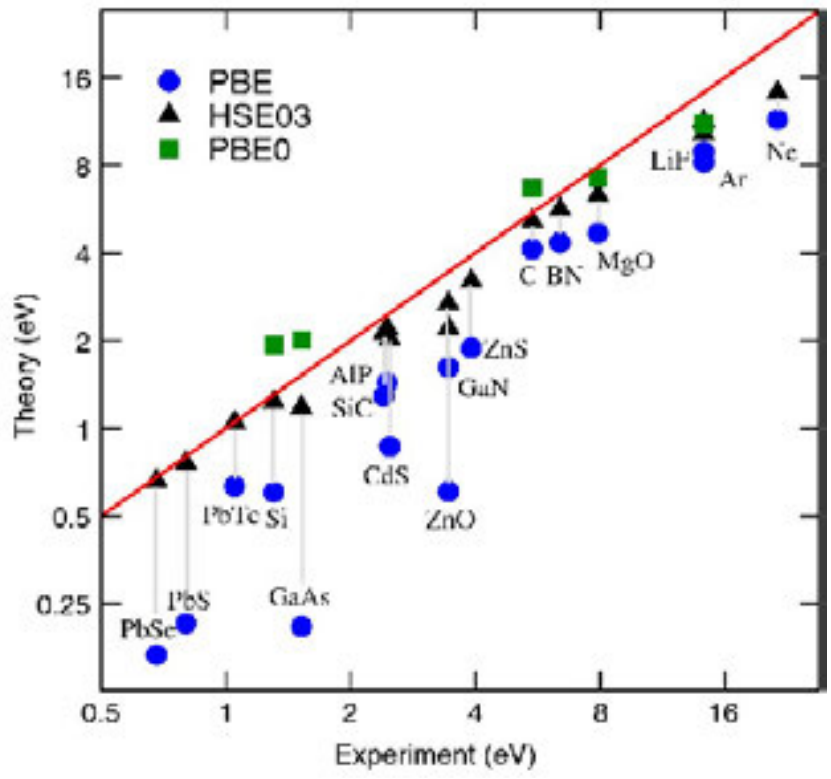
Test case: $SrTiO_3$



	DFT(GGA)	HF	HSE	Expt.
Direct gap (eV) $(\Gamma - \Gamma)$	2.16	4.66	3.8	3.75
CPU time (s)	5	613	324	

DFT vs. PBE0/HSE

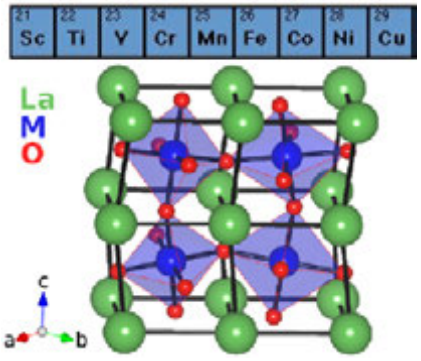
Semiconductors dataset ($\alpha = 0.25$)



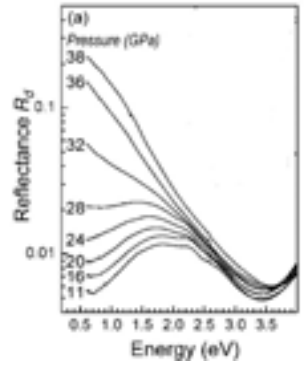
M. Marsman *et al.*, J. Phys.: Condens. Matt. **20** 064201 (2008)

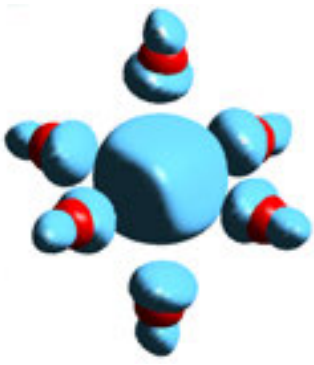
Results

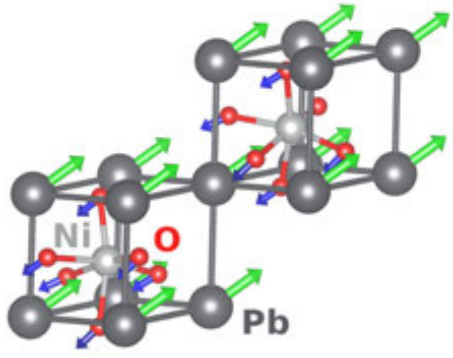
Screened Hybrid Functionals applied to Perovskites

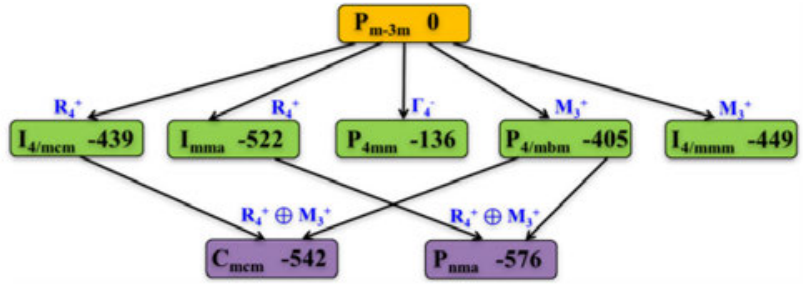


25 **Mn** Manganese 54.938049	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933200
43 **Tc** (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550
75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** 192.217



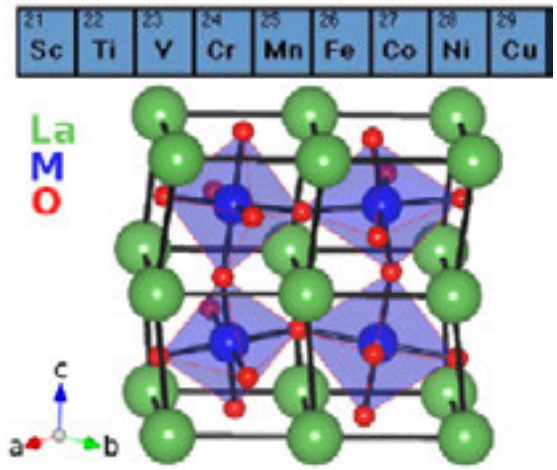






Results: the 3d LaMO$_3$ perovskite dataset

- Band, Mott-Hubbard, charge-transfer insulator
- NM, A/C/G-AFM, PM
- Orthorhombic, Monoclinic, Rhombohedral, Tetragonal
- t_{2g}, e_g: different degree of (de)localization

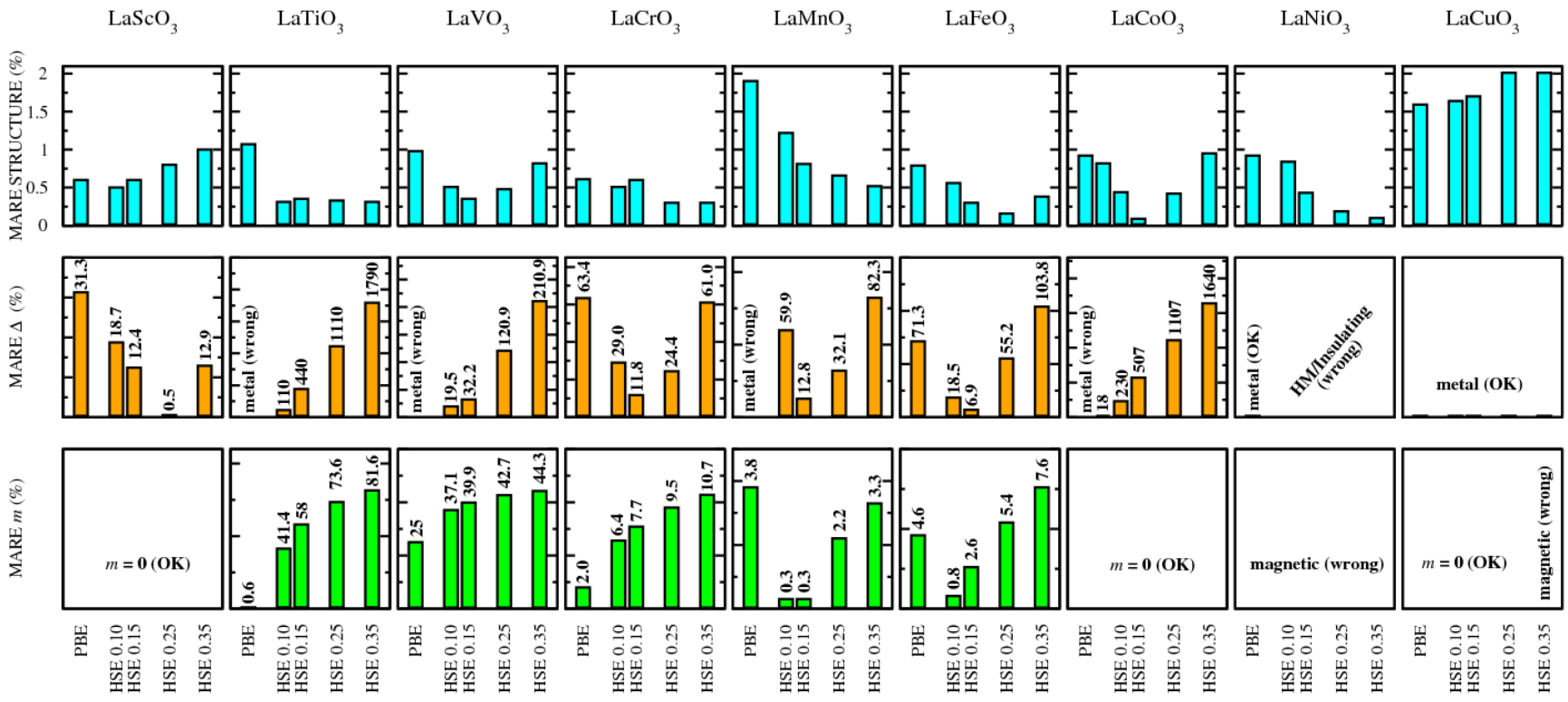


$LaScO_3$	$LaTiO_3$	$LaVO_3$	$LaCrO_3$	$LaMnO_3$	$LaFeO_3$	$LaCoO_3$	$LaNiO_3$	$LaCuO_3$
O	O	M	O	O	O	R	R	T
d^0	↑	↑↑	↑↑↑	↑↑↑ ↑	↑↑↑ ↑↑	↑↓↑↓↑↓	↑↓↑↓↑↓ ↑	↑↓↑↓↑↓ ↑↓
I	I	I	I	I	I	I	M	M
NM	G-AFM	C-AFM	G-AFM	A-AFM	G-AFM	PM	PM	PM

LDA+U: I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. B **53**, 7158 (1996).
HF: T. Mizokawa and A. Fujimori, Phys. Rev. **54**, 5368 (1996).
GW: Y. Nohara, S. Yamamoto, and T. Fujiwara, Phys. Rev. B **79**, 195110 (2009).
HSE: J. He & C. Franchini, Phys. Rev. B **86**, 235117 (2012).

Results: the 3d LaMO$_3$ perovskite dataset

Mean absolute relative value (MARE) based on a fitting of structural properties (volume, lattice parameters, JT/GFO, ion positions), band gap, magnetic moment, spin ordering.



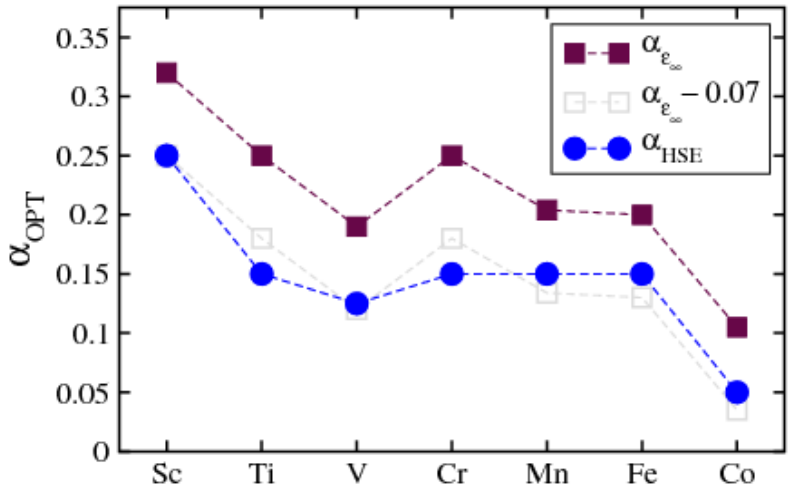
Fitting α

	$LaScO_3$	$LaTiO_3$	$LaVO_3$	$LaCrO_3$	$LaMnO_3$	$LaFeO_3$	$LaCoO_3$	$LaNiO_3$	$LaCuO_3$
α	0.25	0.10 (0.15)	0.10-0.15	0.15	0.15	0.15	0.05	0.0	0.0

Results: the 3d LaMO$_3$ perovskite dataset

Fitting vs $\alpha_{opt} = 1/\epsilon_\infty$

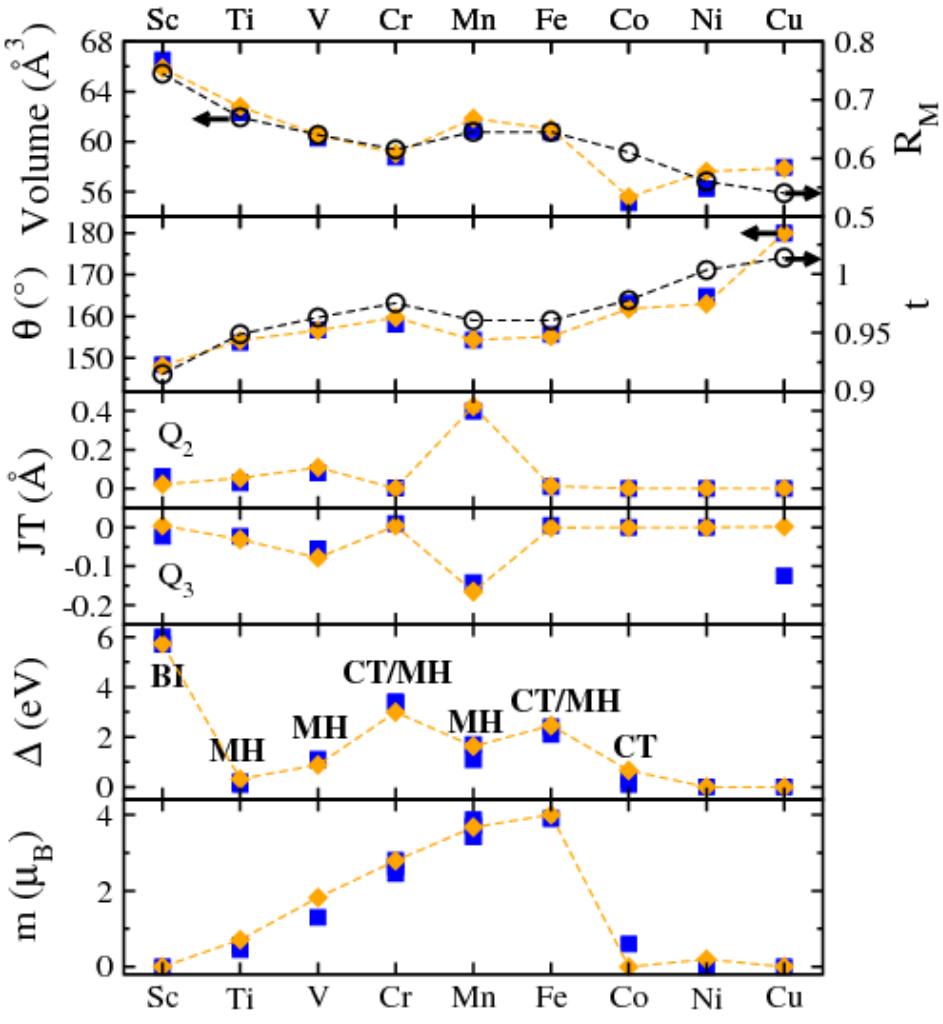
1. $\alpha_{opt}^{\mathrm{HSE}}$ → HSE fitting
2. $\alpha_{opt}^{\epsilon_\infty} = \frac{1}{\epsilon_\infty}$

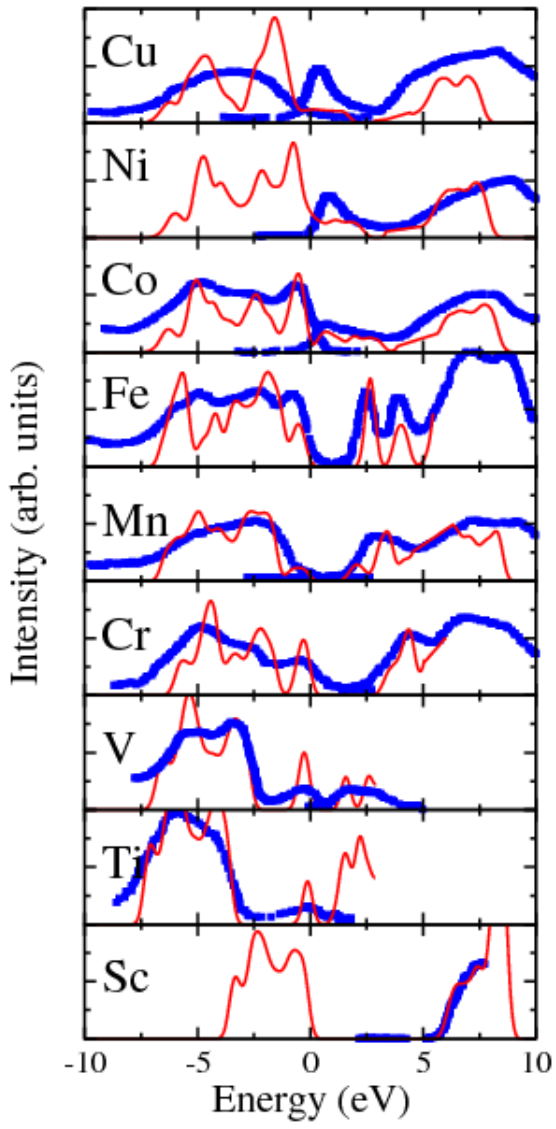


	LSO	LTO	LVO	LCrO	LMO_3	LFO	LCoO	LNO	LCuO
$\alpha_{opt}^{\mathrm{HSE}}$	0.25	0.10/0.15	0.10-0.15	0.15	0.15	0.15	0.05	0	0
$\alpha_{opt}^{\epsilon_\infty}$	0.323	0.125	0.192	0.250	0.204	0.200	0.105	0	0
(ϵ_∞)	(3.1)	(8.0)	(5.2)	(4.0)	(4.9)	(5.0)	(9.5)	∞	∞

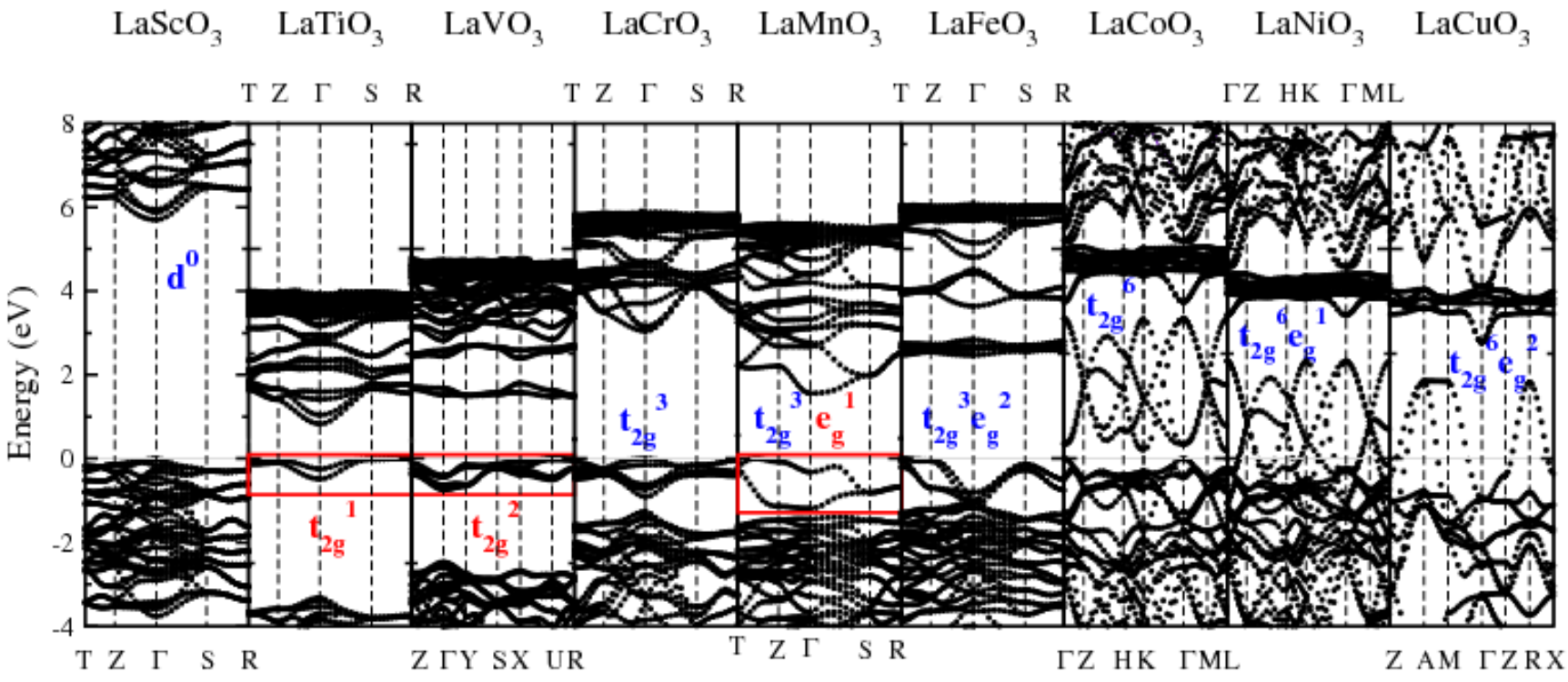
0.07 shift → HSE (screened) already contains some screening (μ)

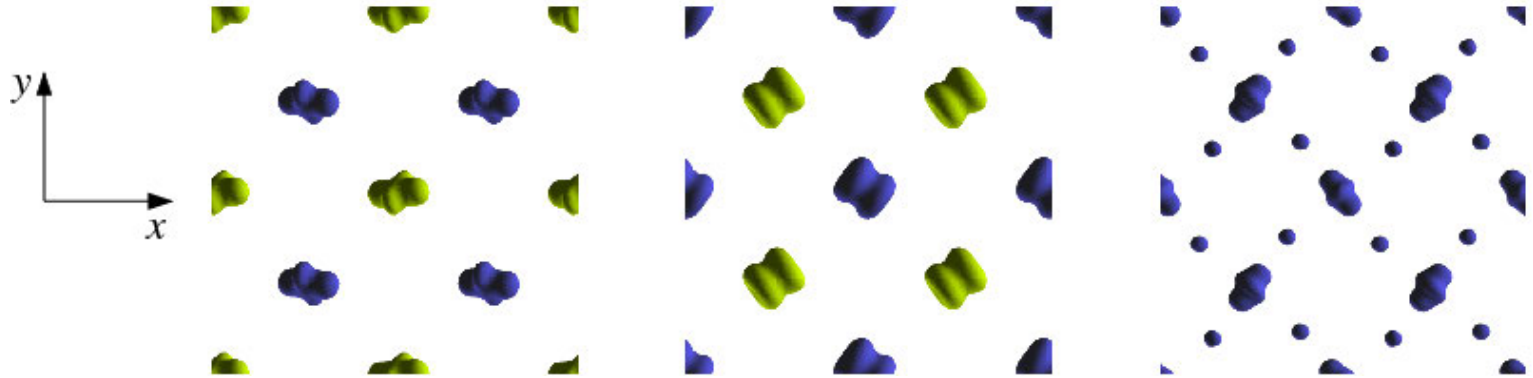
Results: the 3d LaMO$_3$ perovskite dataset





Results: the 3d LaMO$_3$ perovskite dataset

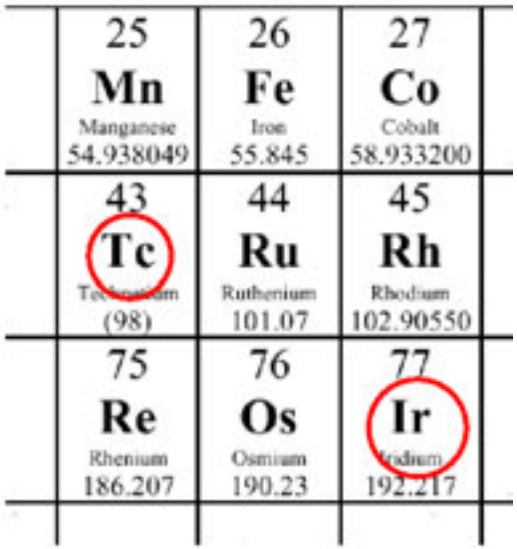




Results: $4d$ and $5d$ perovskites

Larger spatial extension ⇒ Reduced correlation, Metallic & "itinerant magnetism"

But...



- High T_N in $CaTcO_3$ and $SrTcO_3$

  M. Avdeedv *et al.*, JACS **133** 1654 (2011).

  E.E. Rodriguez *et al.*, PRL **106** 067201 (2011).

- insulating state/weak magnetism in $BaIrO_3$

  M.A. Laguna-Marco *et al.*, PRL **105** 216407 (2010).

  R. Arita *et al.*, PRL 108, 086403 (2012).

- Relativistic Mott state in Sr_2IrO_4

  B.J. Kim *et al.*, PRL **101** 076402 (2008).

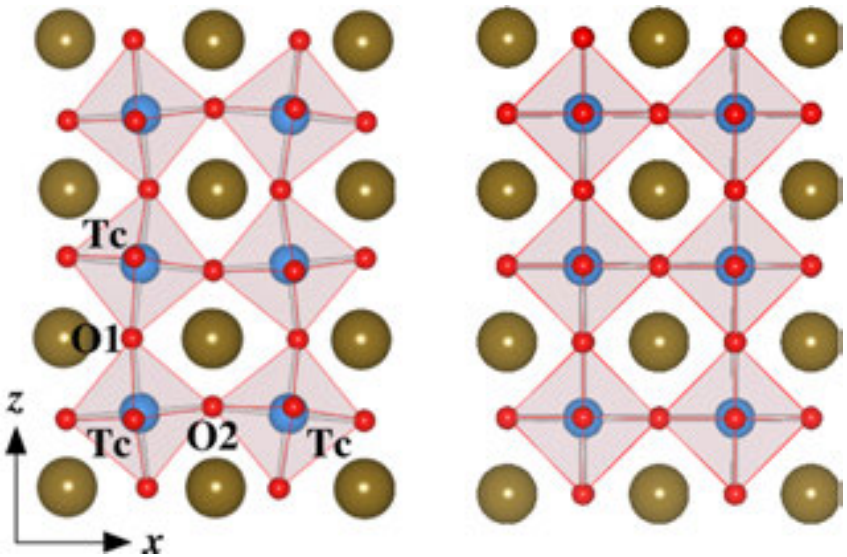
- Magnetic insulator $NsOsO_3$

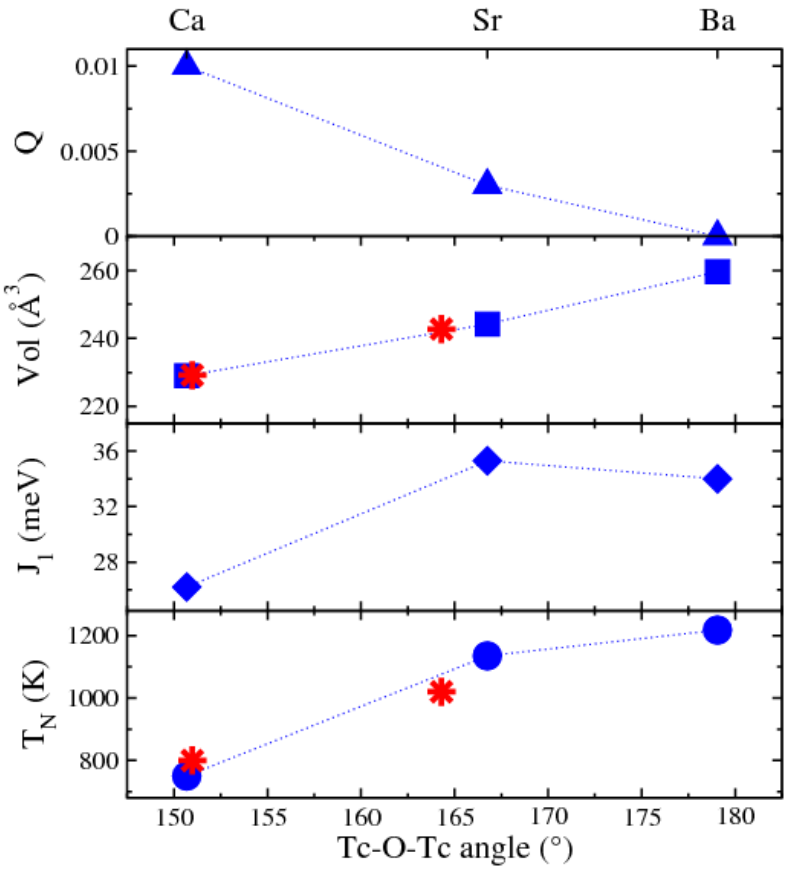
  Y. Shi *et al.* PRB **80**, 161104(R) (2009).

Results: 4d RTcO$_3$ perovskites

HSE total energies	+	$-\sum_{i<j} \mathbf{J}_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$	+	Monte Carlo

R: Ca → Sr → Ba

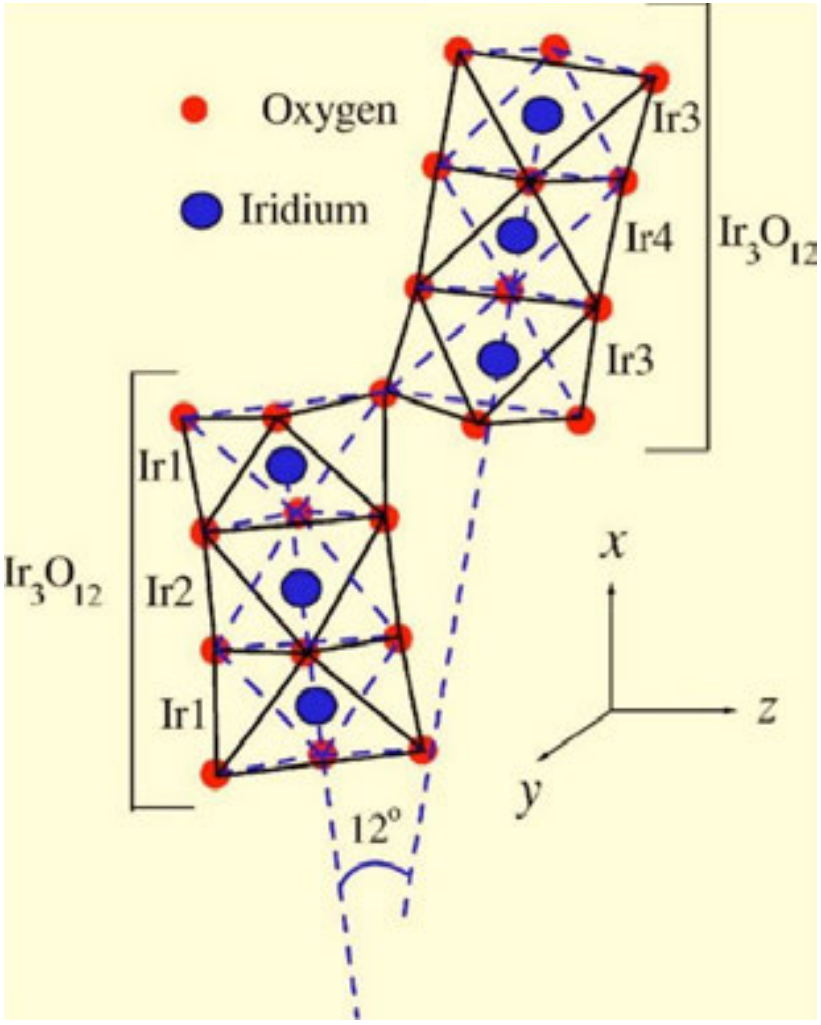




BaTcO$_3$: the highest T$_N$ for compounds without 3d transition metals

C. Franchini, T. Archer, J. He, X.-Q. Chen, A. Filippetti and S. Sanvito, PRB(R) **84**, 115114 (2011)

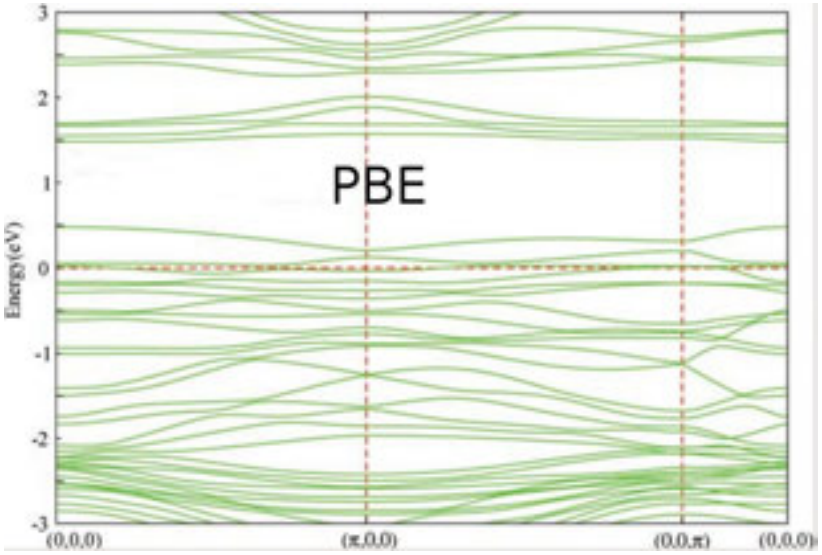
Results: $5d$ $BaIrO_3$ perovskite

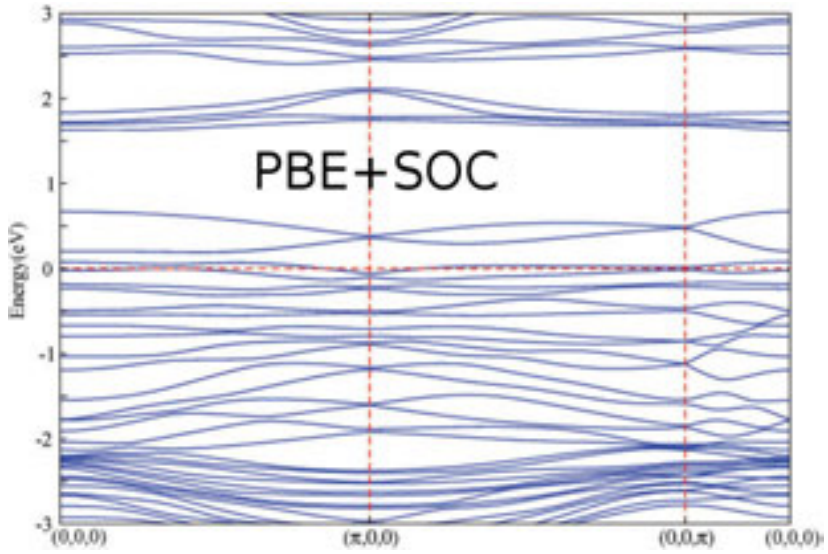


- Quasi 1D
- Weakly ferromagnetic $\mu \approx 0.03\mu_{\mathrm{B}}$
- Nonmetallic (gap $\approx$ 10-50 meV)
- Strong spin-orbit interaction

M. A. Laguna-Marco, *et al.*, PRL **105**, 216407 (2010).

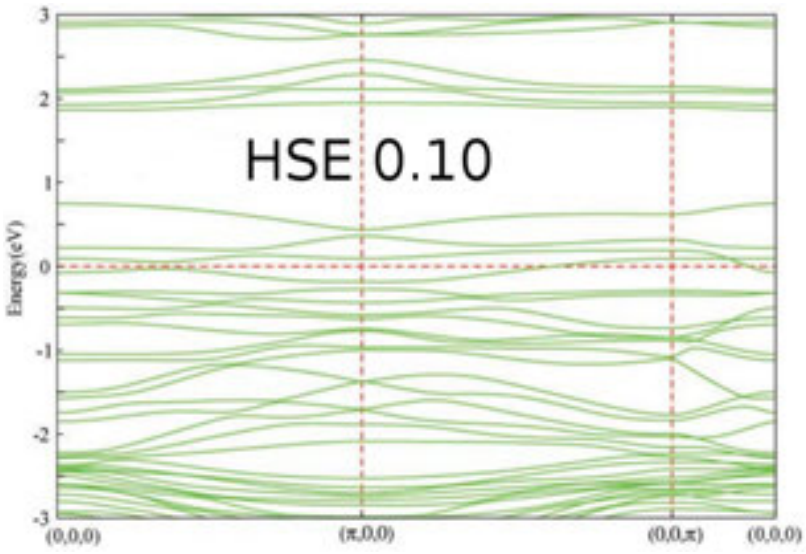
Results: $5d$ $BaIrO_3$ perovskite

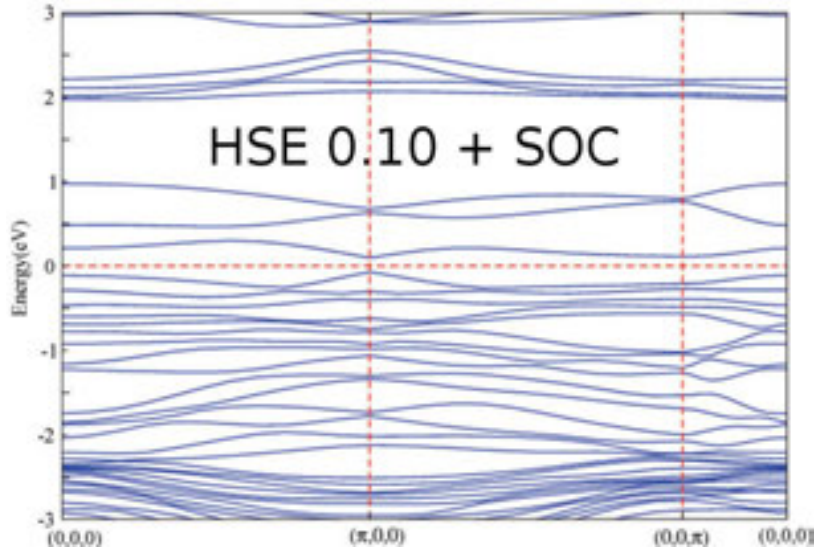




METAL !

Results: $5d$ $BaIrO_3$ perovskite

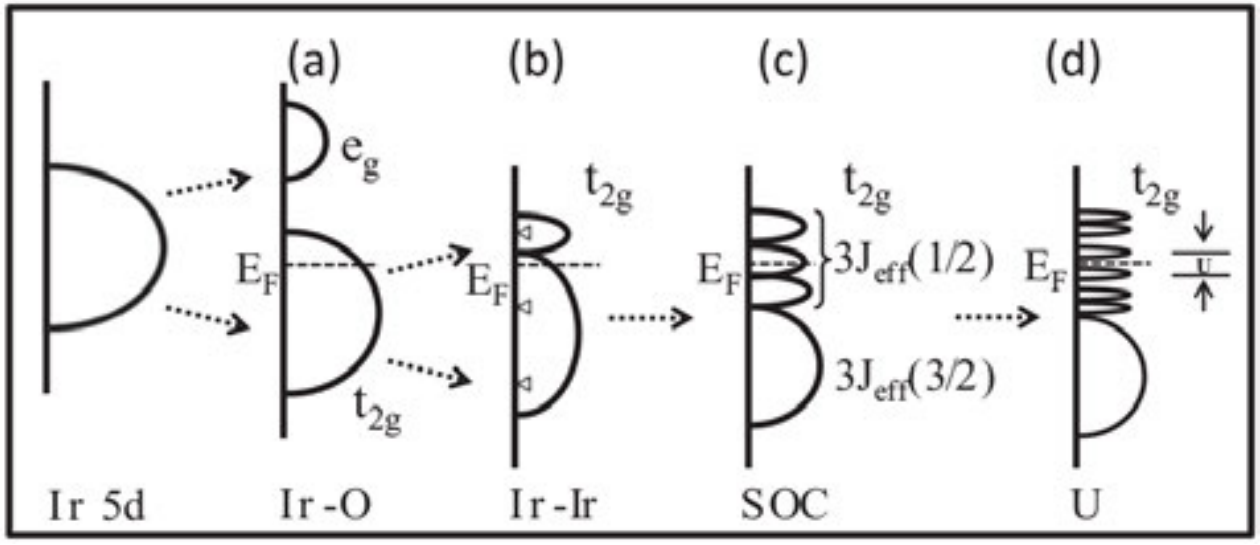




METAL !

INSULATOR, $\mu \approx 0.1\mu_{\mathrm{B}}$

Results: 5d $BaIrO_3$ perovskite



(a) Crystal field splitting: e_g, t_{2g}

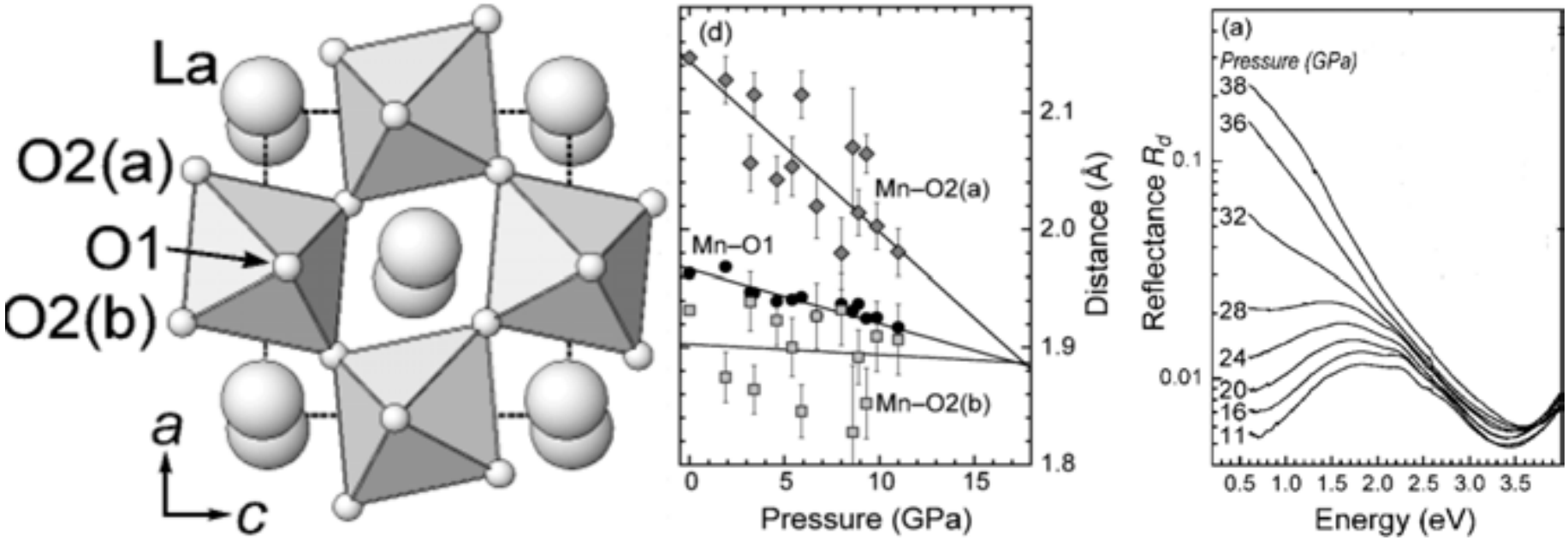
(b) Ir-Ir interaction

(c) Spin-orbit coupling

(e) Moderate U

Weiwei Ju *et al.* PRB **87** 075112 (2013)

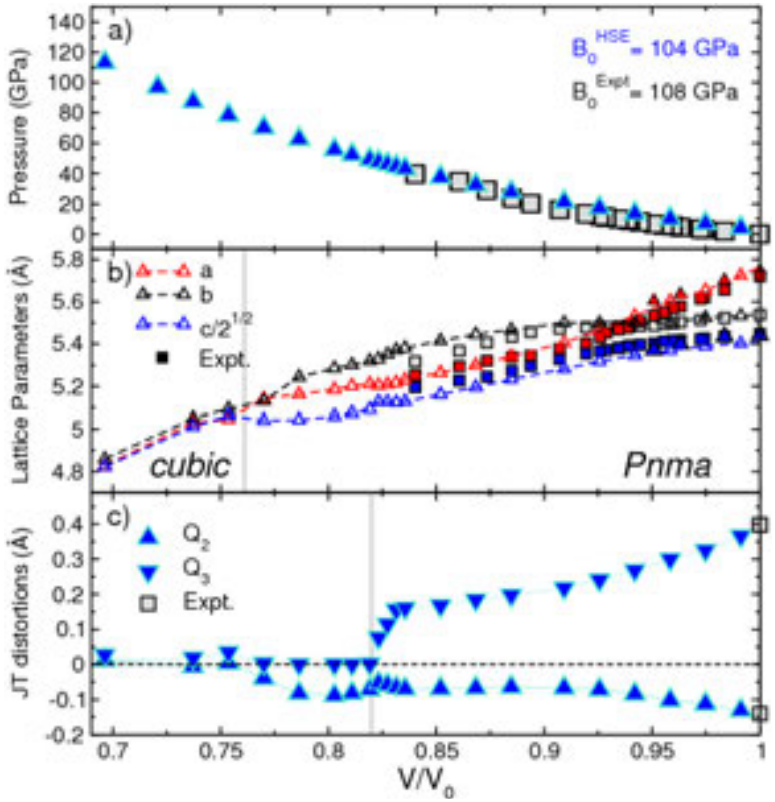
Results: MIT, $LaMnO_3$ under pressure

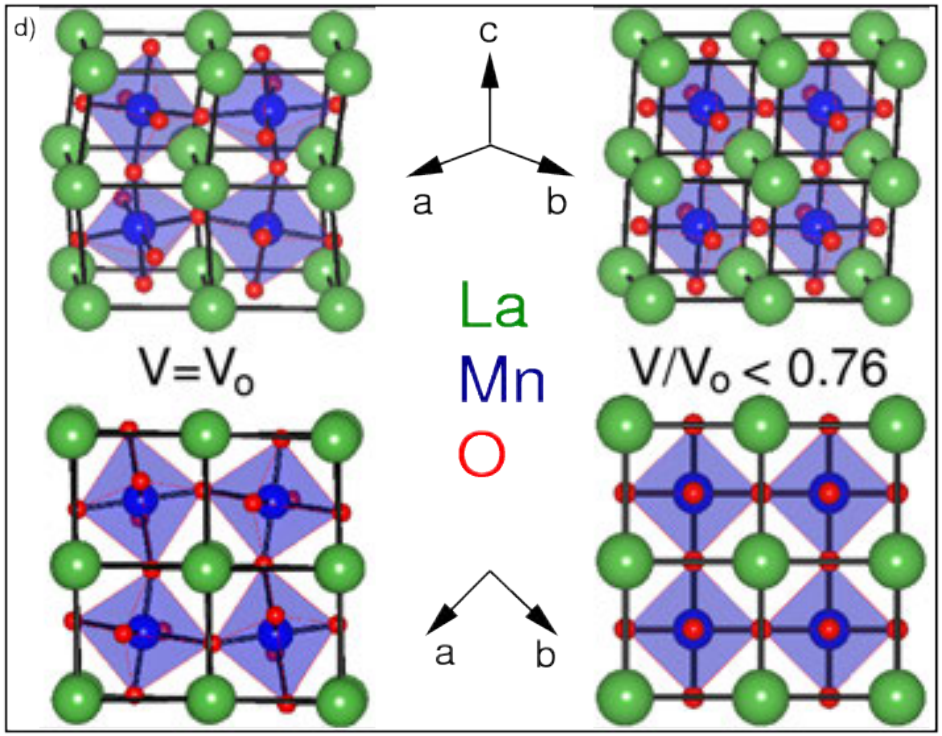


Loa *et al.* PRL **87**, 125501 (2001)

1. Progressive reduction of the JT distortions
2. Insulator to metal transition (Mott ?, i.e. JT distortions in the insulating phase?)

Results: MIT, $LaMnO_3$ under pressure





1. Excellent agreement with Experiment

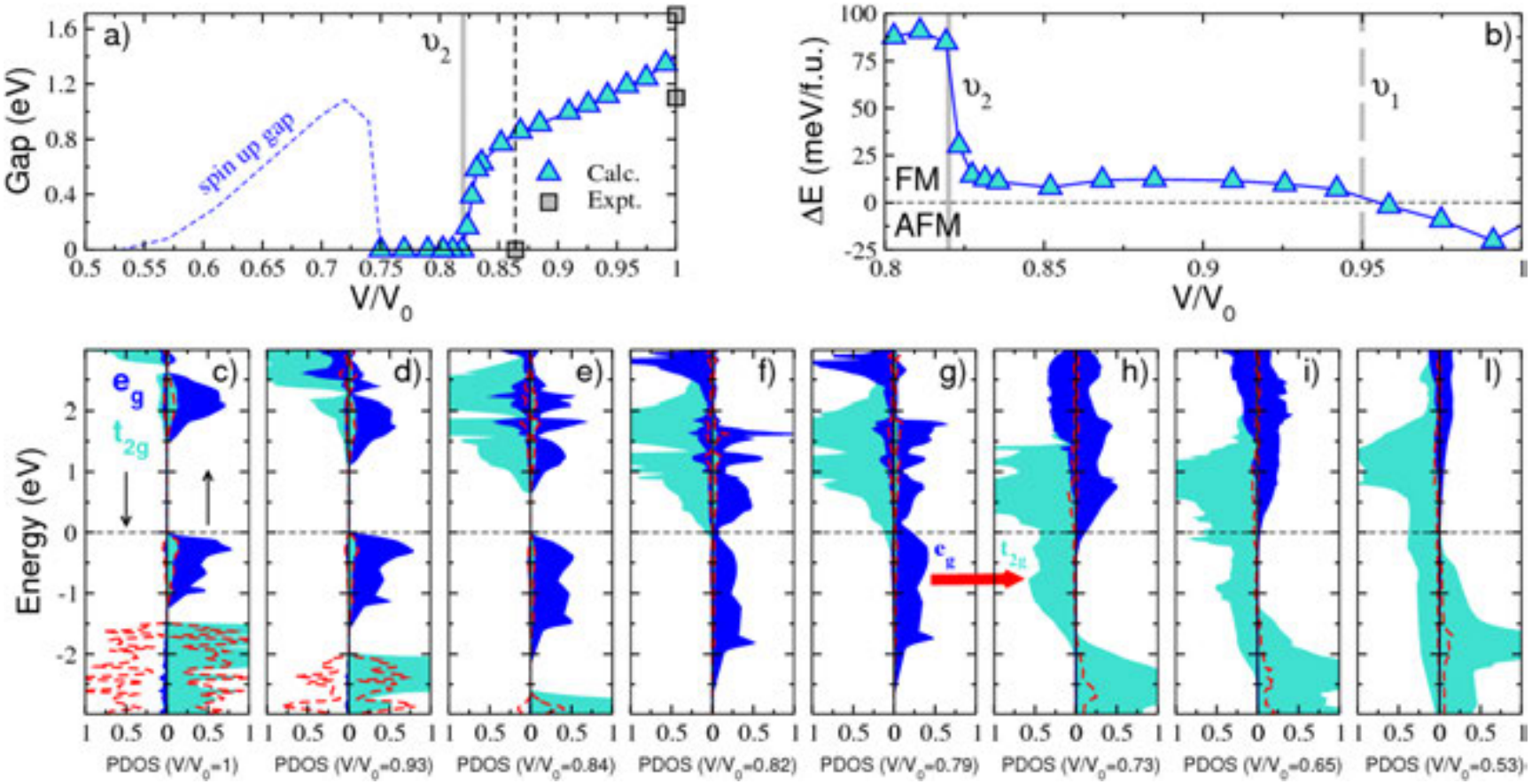
   Loa *et al.* PRL **87**, 125501 (2001); L. Pinsard-Gaudart *et al.* PRB **64**, 064426 (2001)

2. Progressive quenching of JT distortions

3. Orthorhombic to Cubic transition

J. He *et al.* PRB **85** 195135 (2012)

Results: MIT, $LaMnO_3$ under pressure



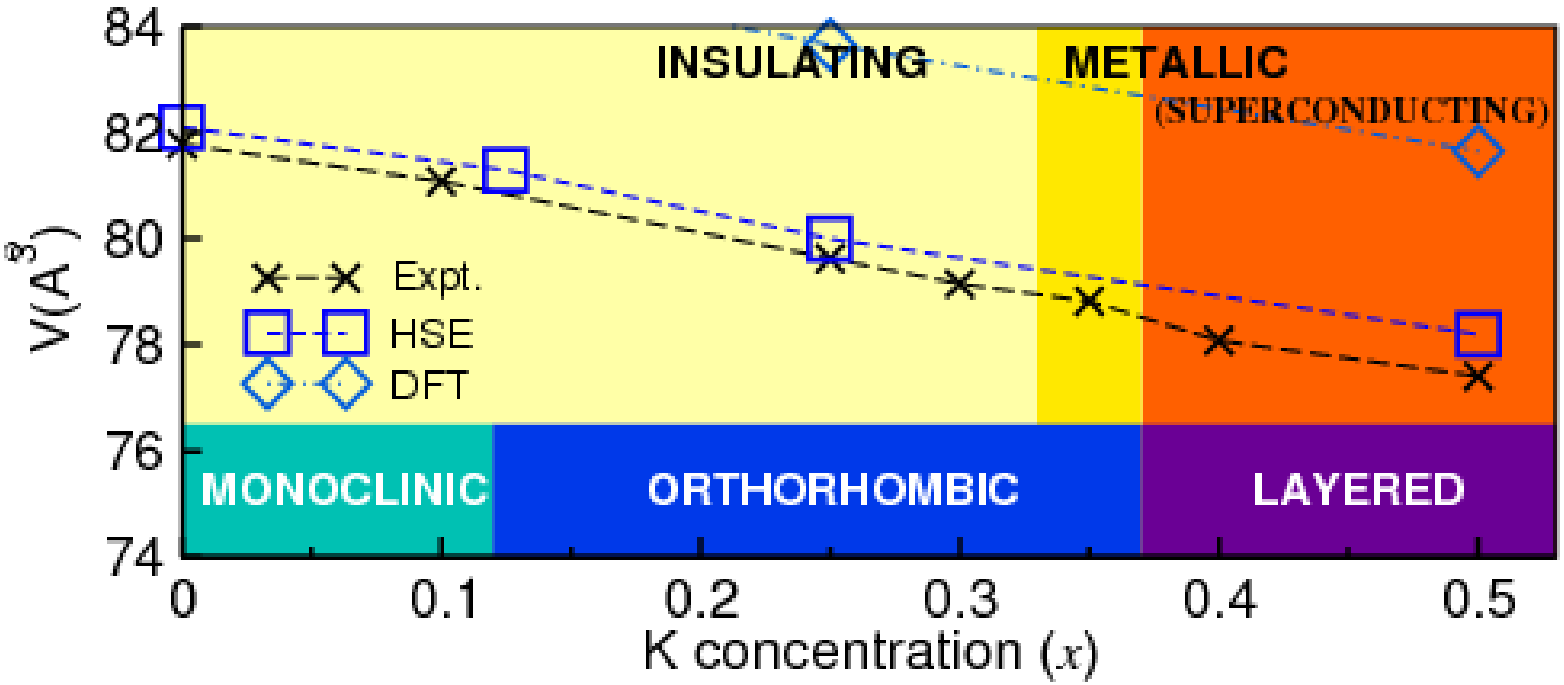
1. V/V_0=0.82 ⇒ non-Mott Insulator to metal transition

   Trimarchi & Binggeli PRB 2005 (LDA+U); Yamasaki *et al.* PRL 2006 (DMFT)

2. Intermediate pressure ⇒ AFM (distorted) FM (undistorted) competition
3. V/V_0=0.70 ⇒ AFM to FM (& Low-spin to High spin) transition

Results: polarons in $BaBiO_3$

hole-doping driven MIT

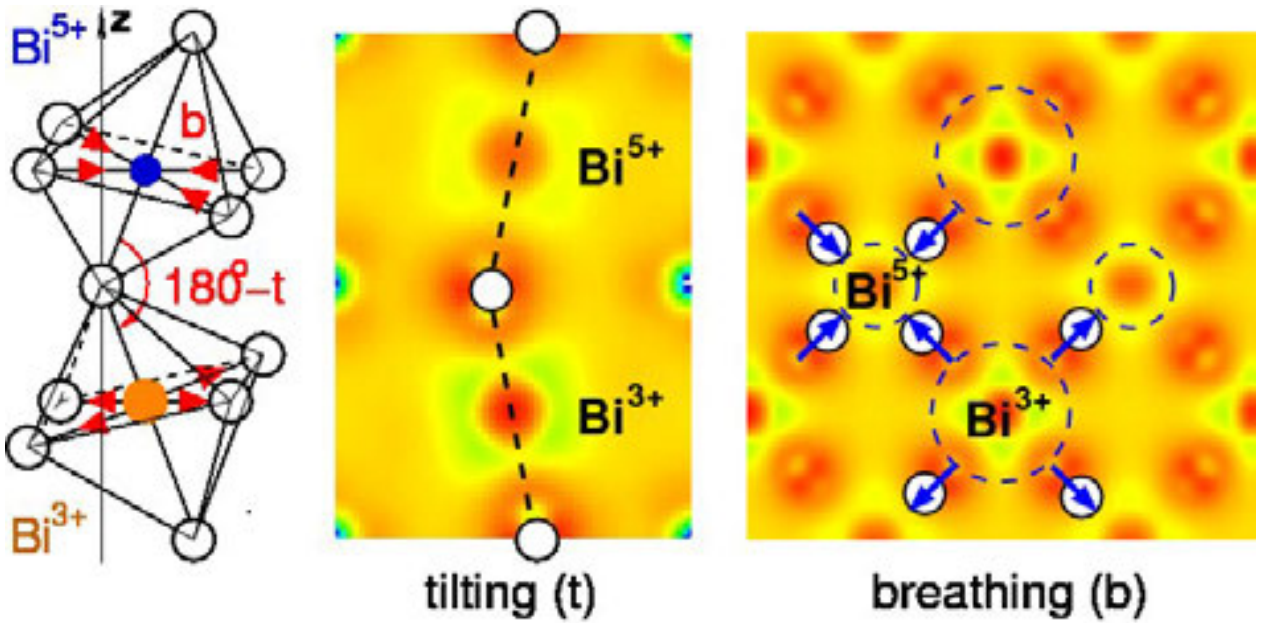


C. Franchini *et al.* PRL 102, 256402 (2009).
C. Franchini *et al.* PRB 81, 085213 (2010).

Results: polarons in $BaBiO_3$

x=0

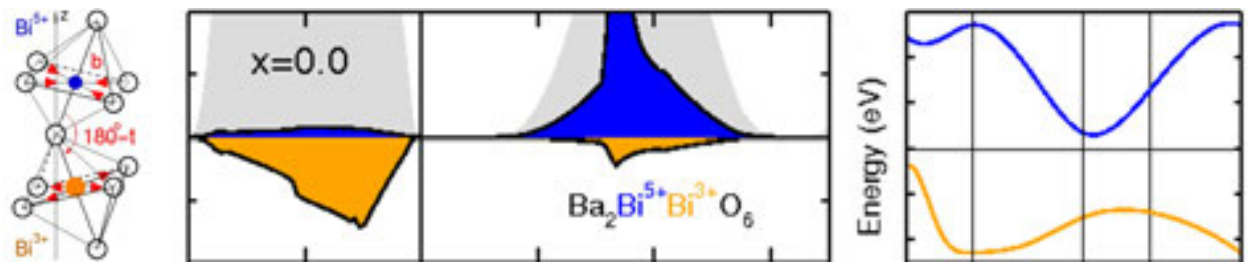
- Valence skipping $\Rightarrow$ Charge disproportionation
  ($Bi^{4+} \Rightarrow Bi^{5+}/Bi^{3+}$, multivalency)
- Structural distortions $\Rightarrow$ breathing (b) and tilting (t) instabilities
- Charged ordered (CDW) insulating state



Results: polarons in $BaBiO_3$

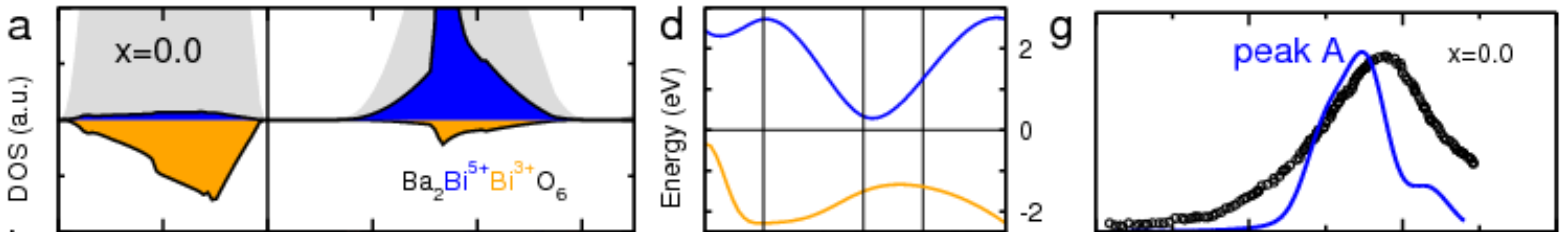
x=0

- Valence skipping $\Rightarrow$ Charge disproportionation
  ($Bi^{4+} \Rightarrow Bi^{5+}/Bi^{3+}$, multivalency)
- Structural distortions $\Rightarrow$ breathing (b) and tilting (t) instabilities
- Charged ordered (CDW) insulating state



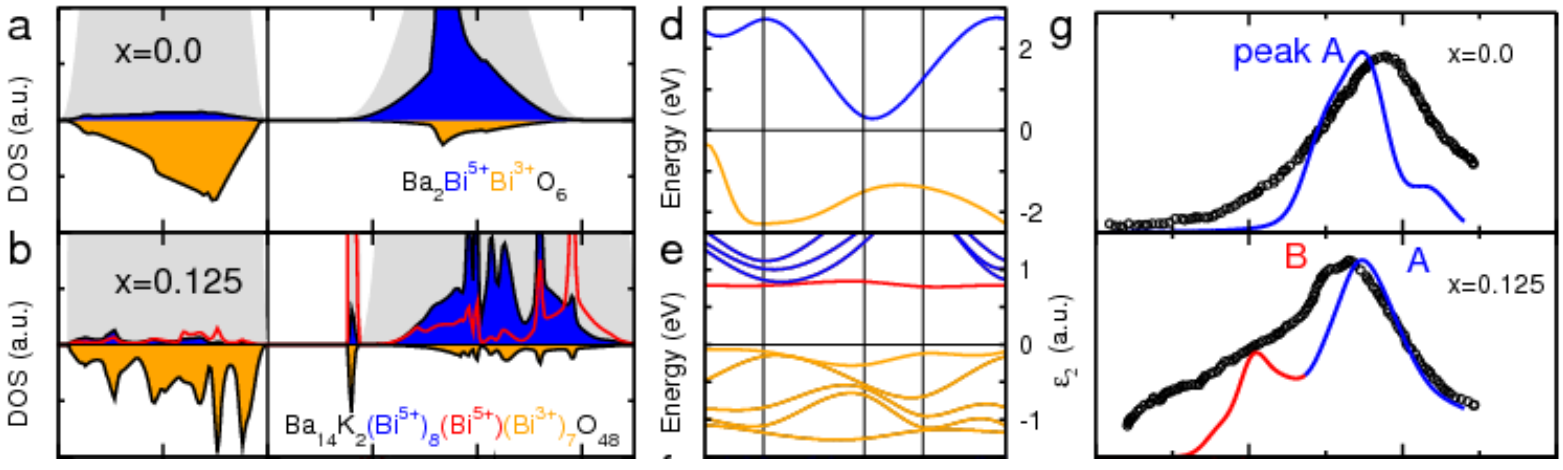
Results: polarons in $BaBiO_3$

$$x > 0$$



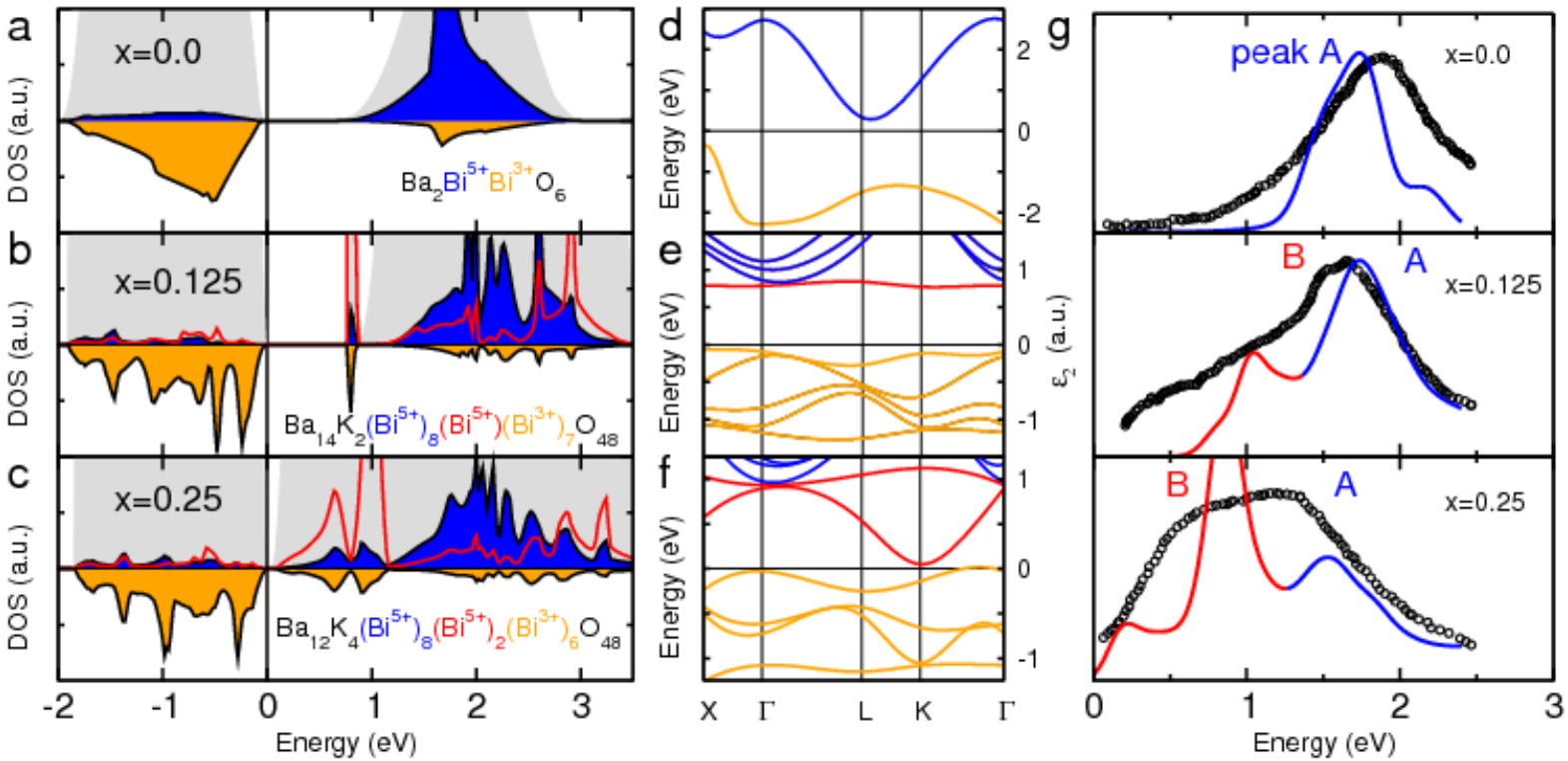
Results: polarons in $BaBiO_3$

$$x > 0$$



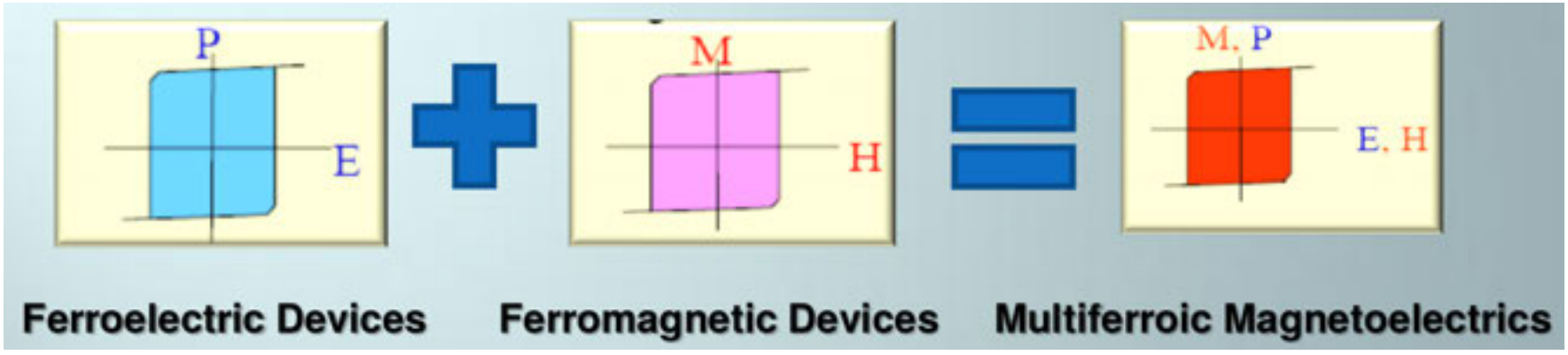
Results: polarons in $BaBiO_3$

$$x > 0$$



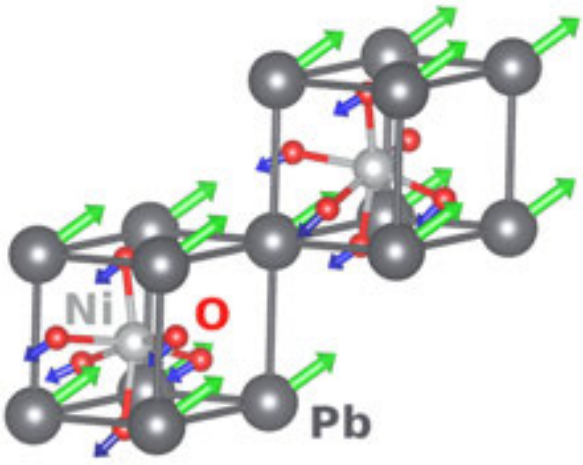
Results: Magnetism + Ferroelectricity

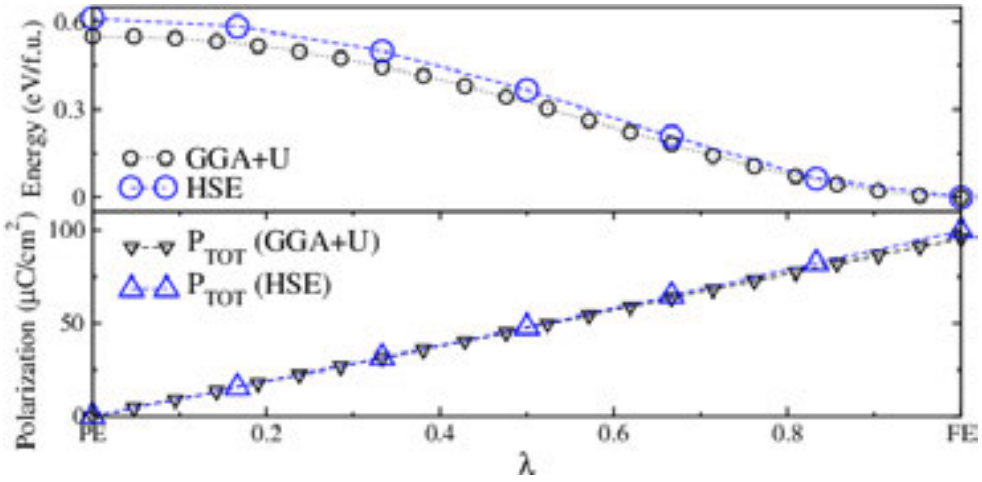
MULTIFERROICS



Results: Magnetism + Ferroelectricity

HSE + modern theory of polarization





$LiNbO_3$-type structure (*R3c*)

Arrows: FE displacements

Total polarization $\mathbf{P}_{\rm tot} \sim 100\ \mu$C/cm^2

Larger then $BiFeO_3$

X. Hao *et al.* PRB 86, 014116 (2012).

Results: Crystal Structure Prediction

HSE + lattice dynamics + Group Theoretical Methods

$SrPdO_3$: New perovskite created in 2010 (Journal of Power Sources **195** 3806)

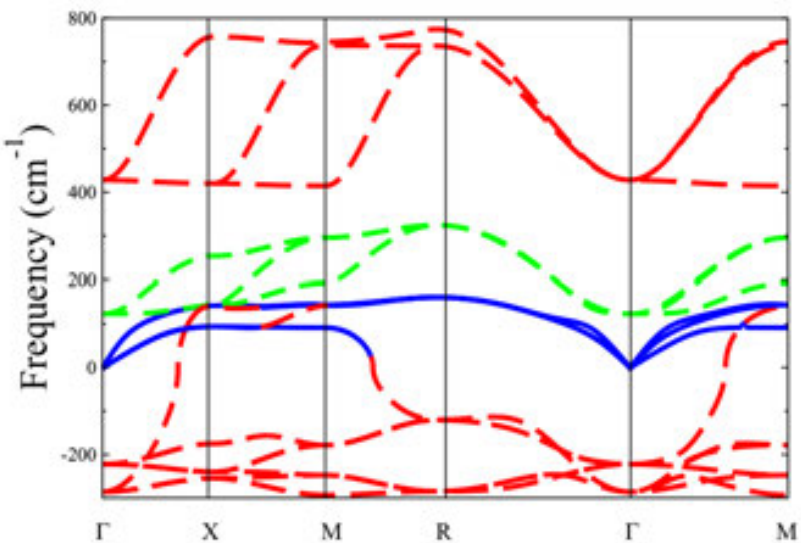
J. He & C. Franchini PRB 89, 045104 (2014).

Results: Crystal Structure Prediction

HSE + lattice dynamics + Group Theoretical Methods

$SrPdO_3$: New perovskite created in 2010 (Journal of Power Sources **195** 3806)

Structure: Unknown (t=0.905 → cubic phase unstable)

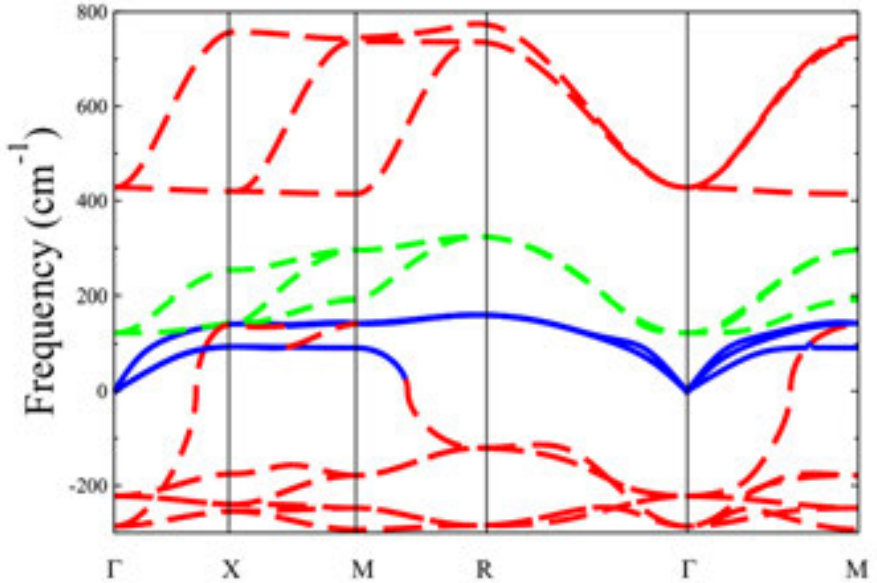


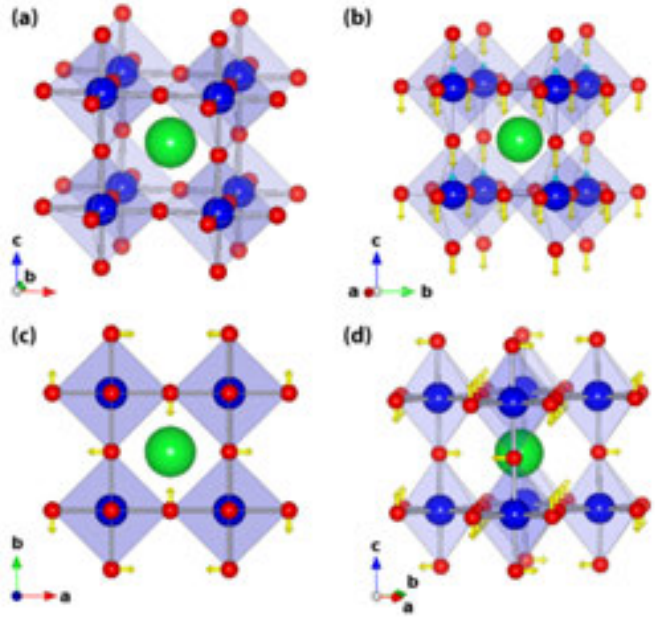
Strategy: stabilization of the negative modes (Γ_4^-, M_3^+, R_4^+) through atomic displacements.

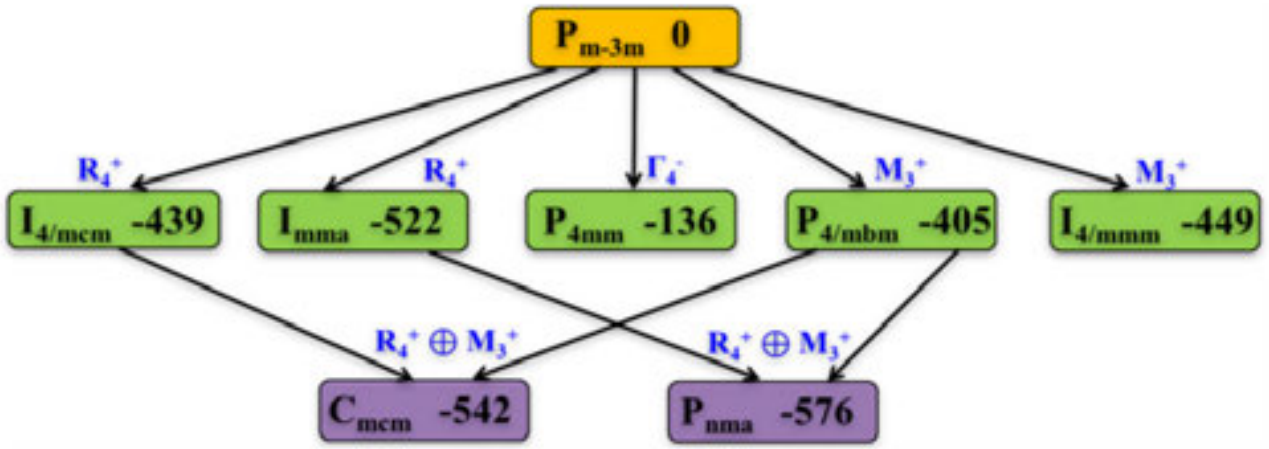
J. He & C. Franchini PRB 89, 045104 (2014).

Results: Crystal Structure Prediction

P_{nma}







Summary

$$\left(-\frac{1}{2}\Delta + V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r}) + V_{\rm xc}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r})$$

$$+$$

$$\left(-\frac{1}{2}\Delta + V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int V_{\rm X}(\mathbf{r},\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}'$$

$$=$$

$$\left(-\frac{1}{2}\Delta + V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r}) + V_{\rm c}(\mathbf{r}) + \alpha V_{\rm x}^{lr}(\mathbf{r}) + (1-\alpha)V_{\rm x}^{sr}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int \alpha V_{\rm x}^{sr}(\mathbf{r},\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}'$$

$$\approx$$

$$\left(-\frac{1}{2}\Delta + V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}',E_{n\mathbf{k}})\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}'$$

Hybrid functionals for materials science: accurate and predictive