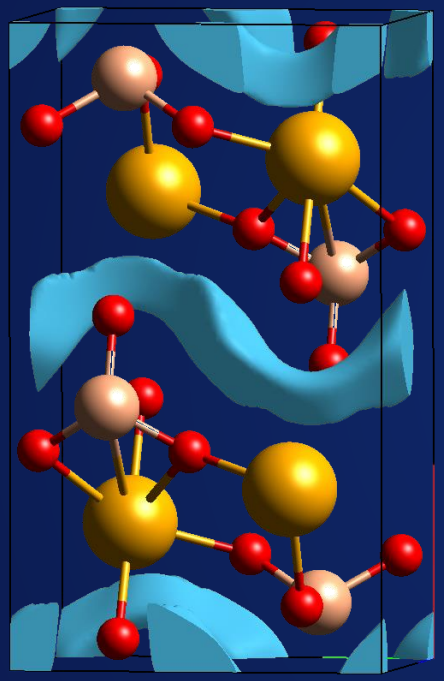

How Battery Materials Work: Visualizing Ion Migration

Mette Ø. Filsø, Aarhus University, Denmark

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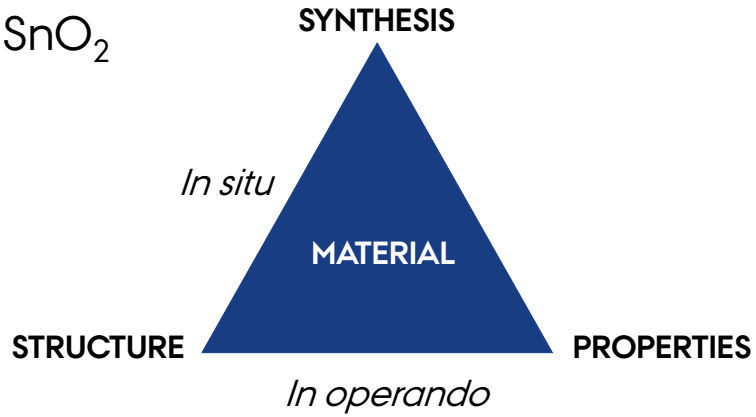
BATTERY RESEARCH AT AARHUS UNIVERSITY

- Synthesis and characterization of electrode materials
  - $Li_4Ti_5O_{12}$, $LiFePO_4$, $LiCoO_2$, $LiMn_2O_4$, TiO_2, SnO_2
  - $Na_xMn_yCo_zNi_{1-y-z}O_4$
- Nanostructuring
- Performance testing of half-cells
- *In operando* X-ray diffraction
- *In situ* X-ray diffraction
- Visualization of ion migration
- MOFs



Laumann *et al., Solid State Ionics* **181** (2010), 1525-1529
Laumann *et al., J. Inorg. Chem.* **14** (2011), 2221-2226
Jensen *et al., JACS* **134** (2012), 6785-6792
Laumann *et al., J. Electrochem. Soc.* **159** (2012), A166
Lock *et al. Dalton T.* **42** (2013), 9555-9564





Jensen *et al., Chem. Mater.* **25** (2013), 2282-2290
Shen *et al., Chem. Mater.* **25** (2013), 5023-5030
Shen *et al., Chem. Mater.* **26** (2014), 3679-3686
Birgisson *et al., Dalton T.* **43** (2014), 15075-15084
Eikeland *et al. Inorg. Chem.* **53** (2014), 10178-10188
Shen *et al. Rev. Sci. Inst.* **85** (2014), 104103
Søndergard *et al. Chem. Mater.* **27** (2015), 119-126

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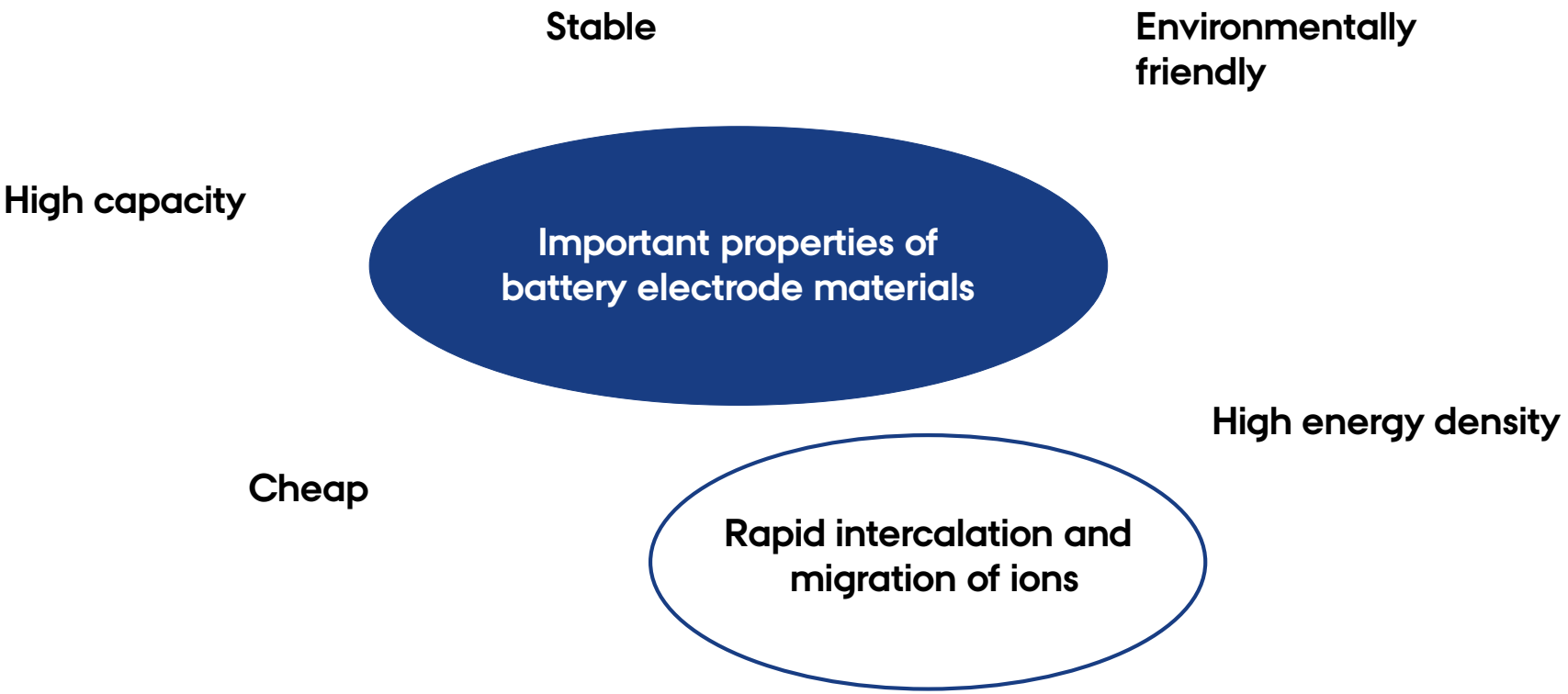
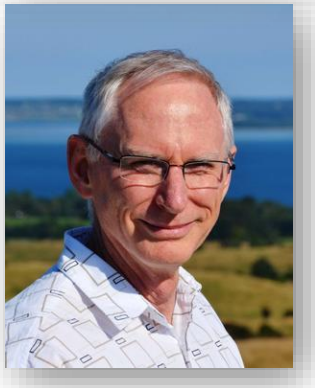
INTRODUCTION



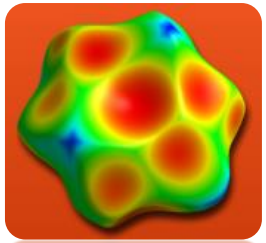
THE PROCRYSTAL ANALYSIS



The Procrystal Analysis is performed with the software CrystalExplorer.

Procrystal

Unit cell dimensions
Space group
Atomic positions



$$\rho_{pro}(r) = \sum_{A \in crystal} \rho_A(r)$$

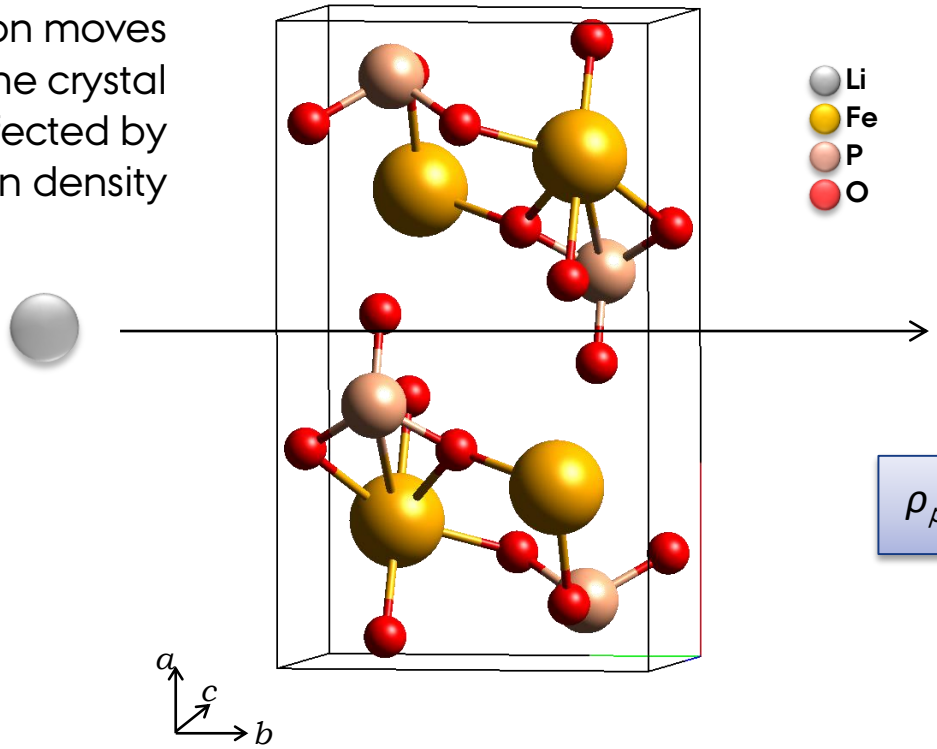
Ball-and-stick model → **Continuous landscape of electron density**

Spackman and McKinnon, *CrystEngComm.* **11** (2009), 19-32

THE PROCRYSTAL ANALYSIS

$LiFePO_4$

When the ion moves through the crystal structure, it is affected by the electron density

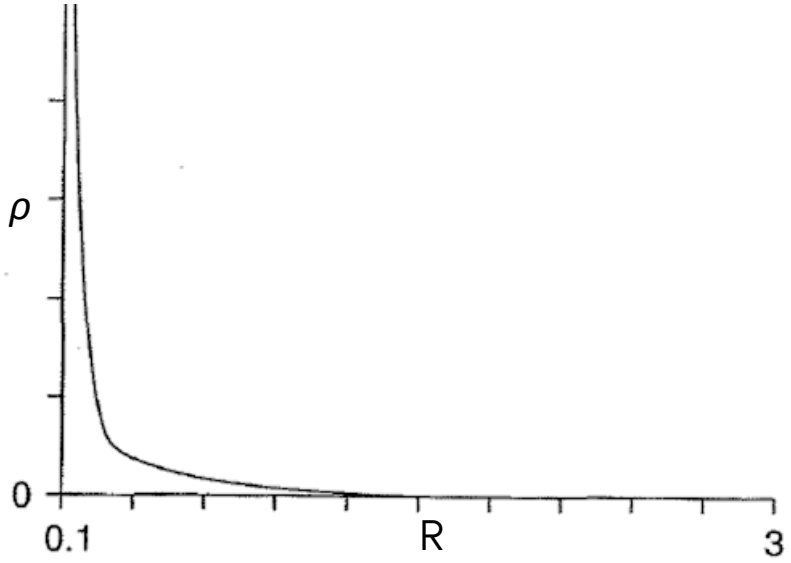


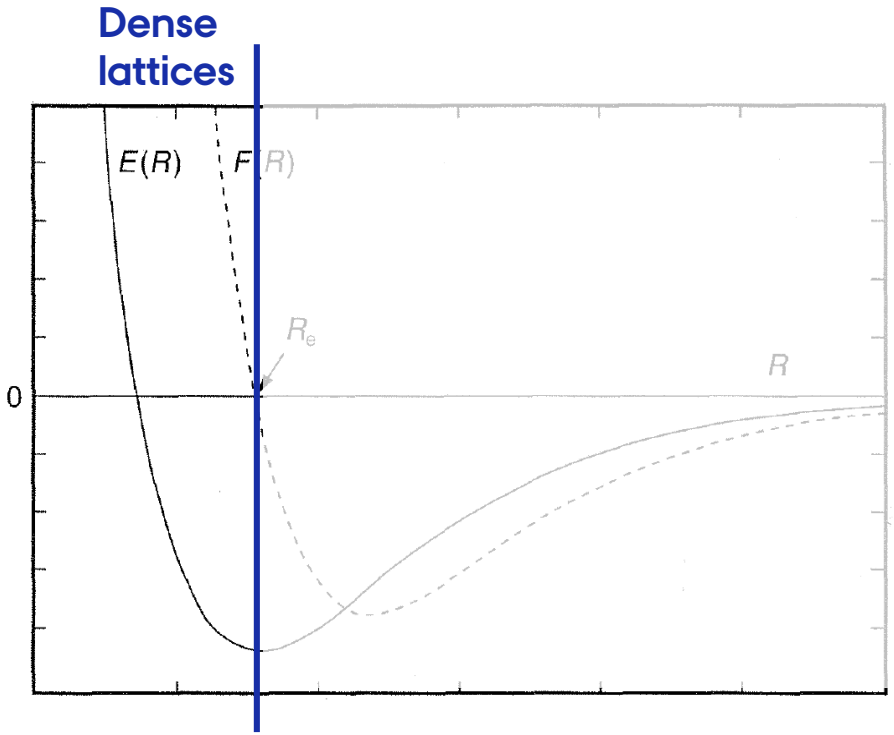
The ion will choose the path of lower electron density.

ρ_{pro} ⟶ Ion migration

THE PROCRYSTAL ANALYSIS

Electron density = Potential energy?
For dense lattices there is a clear similarity between curves!





Popelier 'Atoms in molecules: an introduction', *Prentice Hall*, PTR (2000),

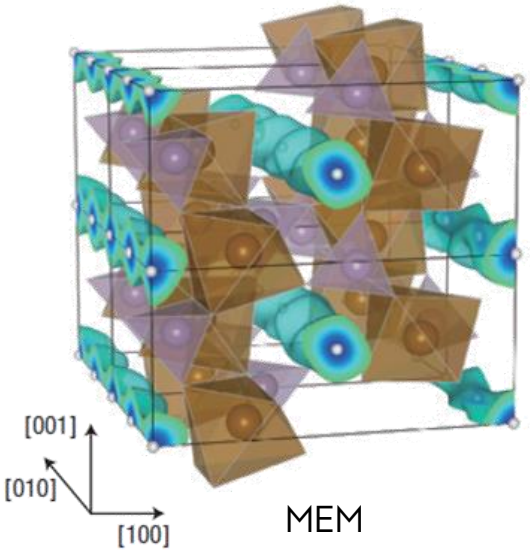
THE PROCRYSTAL ANALYSIS

Limitations:

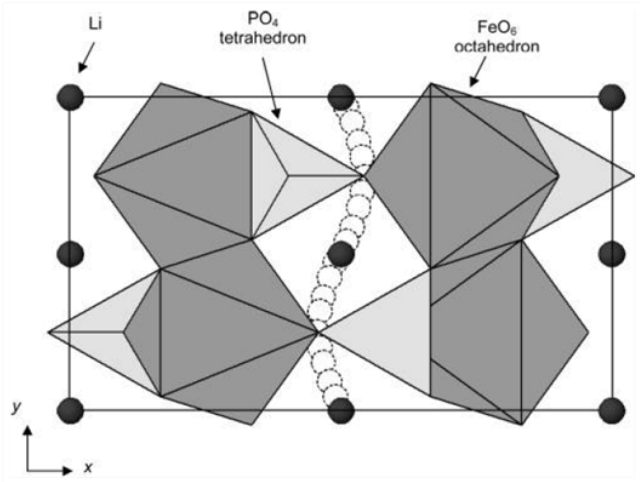
1) Does *not directly* account for Li…Li interactions, or Li…framework interactions
2) Static lattice
3) Analysis depends on the CIF used
4) Relies on the *electron density = potential energy* assumption
5) Neutral atoms

RESULTS

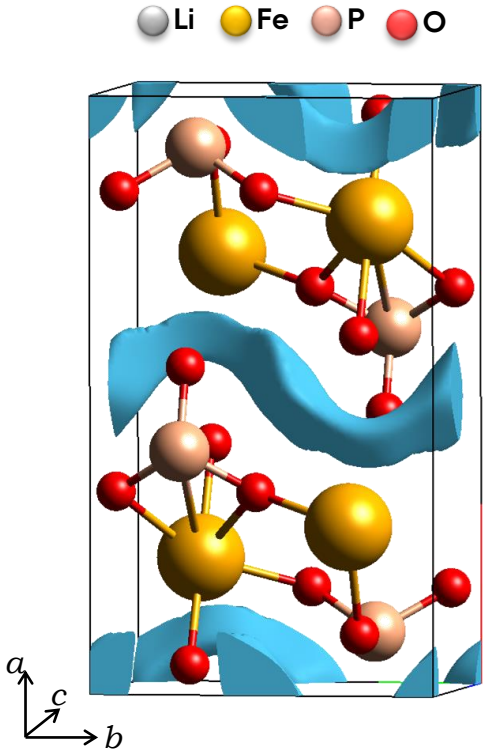
$LiFePO_4$



MEM



Atomistic modeling



Procrystal calculation

ρ_{pro} = 0.0030 au
ρ_{pro}(migration) = 0.0027 au

Islam *et al.*, *Chem. Mater.* **17** (2005), 5085-5092
Nishimura *et al.*, *Nature mat*, **7** (2008), 707-711

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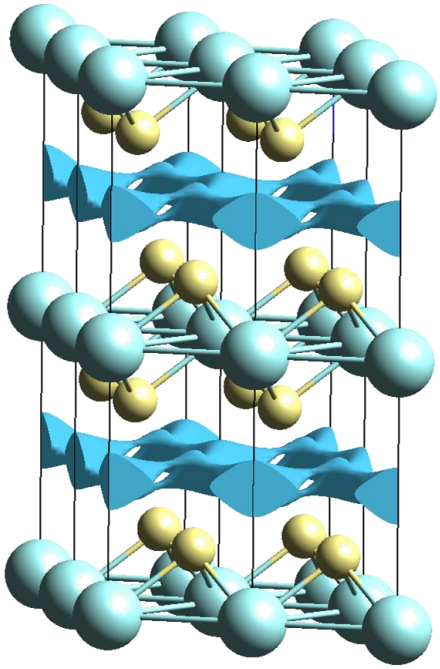
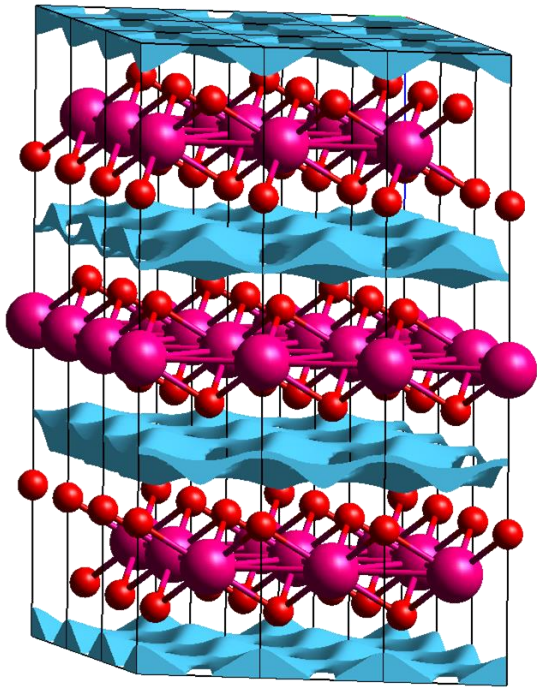
RESULTS

$LiTiS_2$



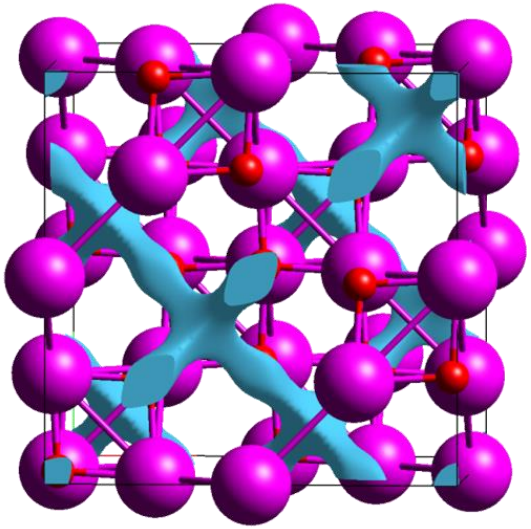
ρ_{pro} = 0.0042 au
ρ_{pro}(migration) = 0.0042 au

$LiCoO_2$



ρ_{pro} = 0.0060 au
ρ_{pro}(migration) = 0.0058 au

$LiMn_2O_4$



ρ_{pro} = 0.0040 au
ρ_{pro}(migration) = 0.0033 au

RESULTS

Dimensionality	Compounds			
1D	$LiAlPO_4F$	$LiFePO_4$	$LiFeBO_3$	
2D	$LiTiS_2$	$LiCoO_2$	$LiMnO_2$	$LiFeP_2O_7$
3D	$Li_4Ti_5O_{12}$	$LiTi_2O_4$	$LiMn_2O_4$	$Li_2Mn_2O_4$
	$Li_6Si_2O_7$	Li_6PS_5I	$LiFeSO_4F$	Li_5AlO_4-α
	Li_2SiO_3	$Li_{1.8}SnO_3$	Li_4GeS_4	$Li_3Fe_2(PO_4)_3$
	$Li_2Ge_2O_5$	$Li_4P_2O_7$	Li_2TiO_3	$Li_3V_2(PO_4)_3$
	Li_3AuO_3	Li_3BO_3		

Procrystal value for rapid Li-ion migration:

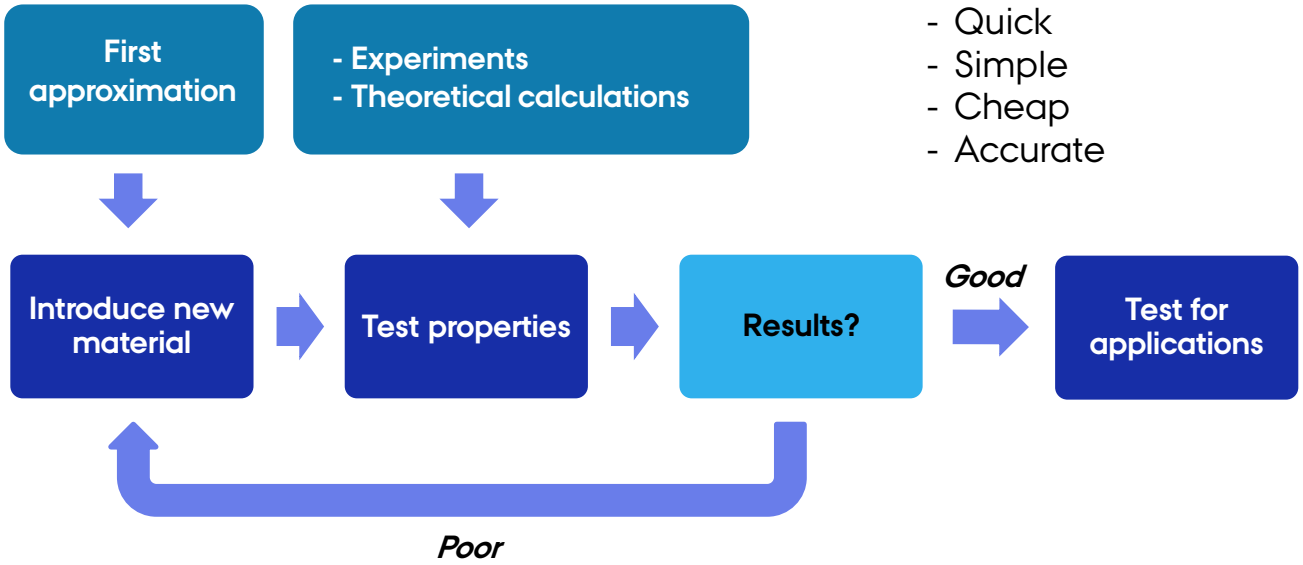
ρ_{pro}(migration) = **0.0029(7) au**

NB: for layered materials:

ρ_{pro}(migration) = **0.0054(9) au**

APPLICATIONS

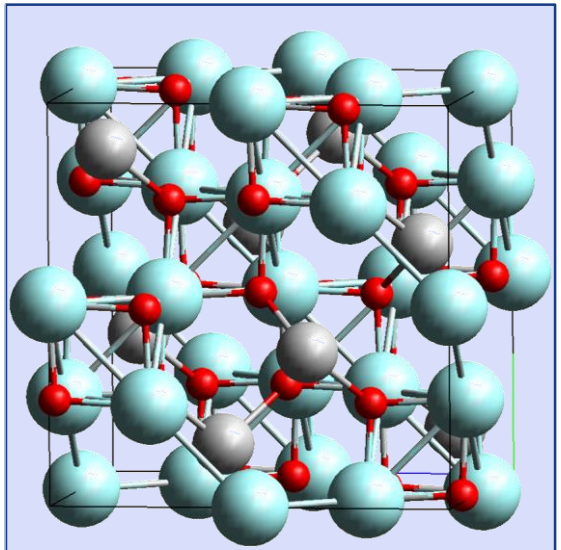
1) Educational tool
2) Visual addition to scientific communication
3) 'first approximation tool'



First approximation tool:
- Quick
- Simple
- Cheap
- Accurate

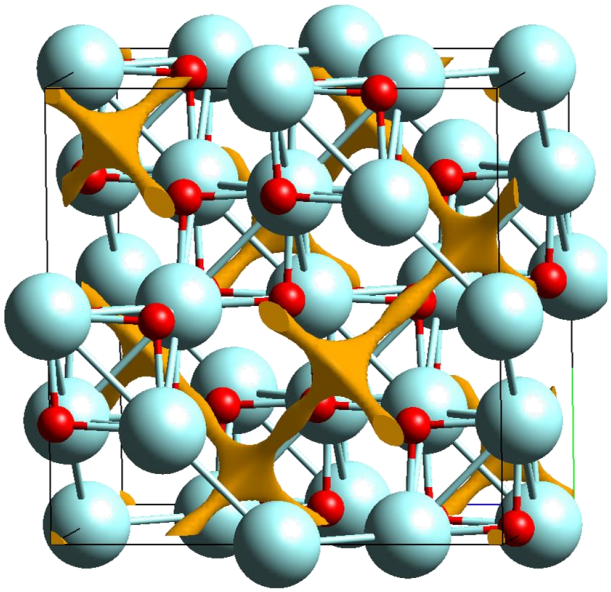
TREATING ATOMIC DISORDER

$Li_4Ti_5O_{12}$



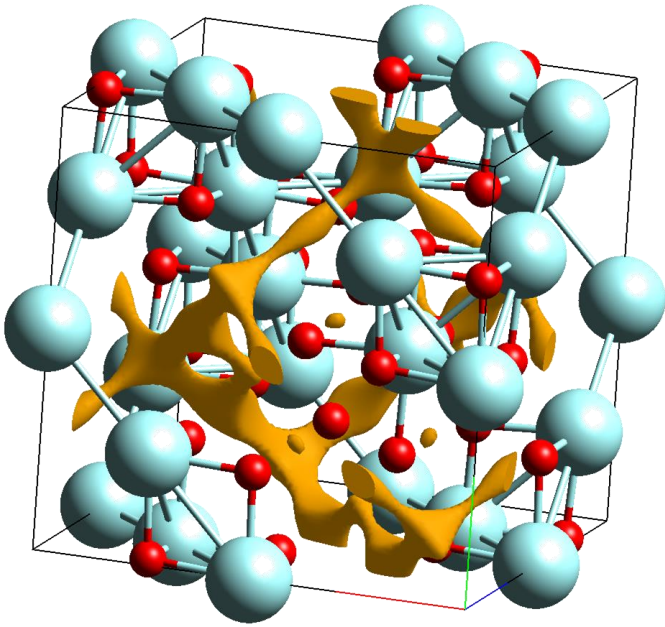
8*a* site: Li
32*e* site: O
16*d* site: 1/6 Li, 5/6 Ti

'densest framework'



ρ_{pro}(migration) = 0.0040 au

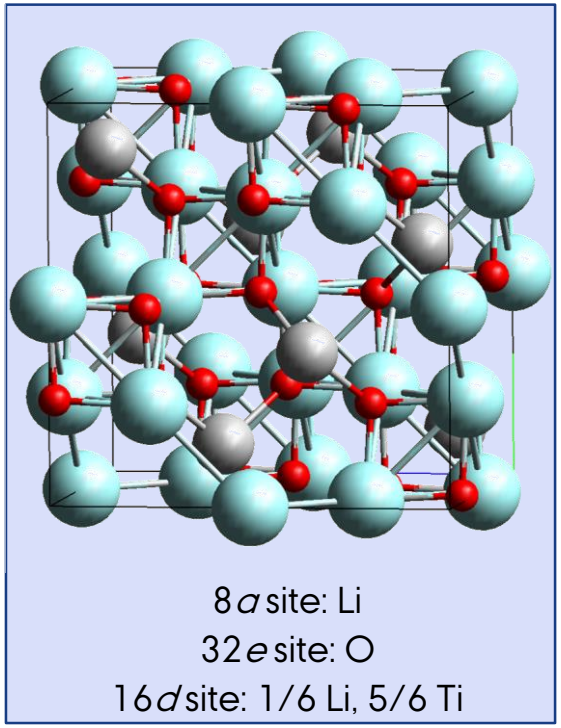
'actual stoichiometry'



ρ_{pro}(migration) = 0.0035 au

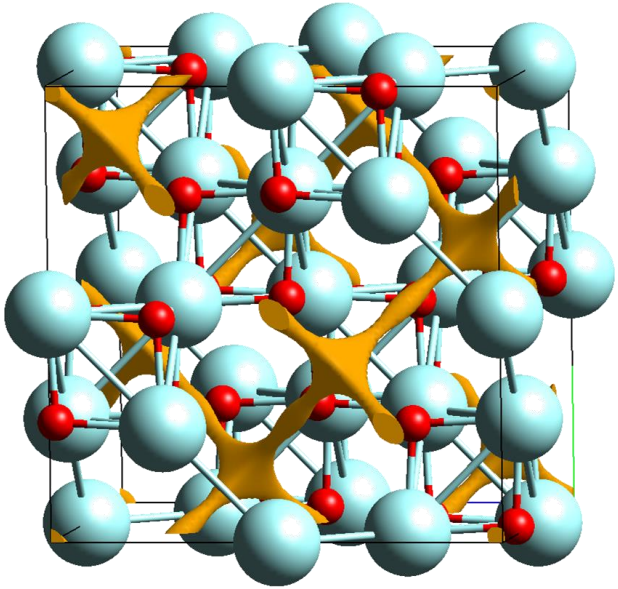
TREATING ATOMIC DISORDER

$Li_4Ti_5O_{12}$



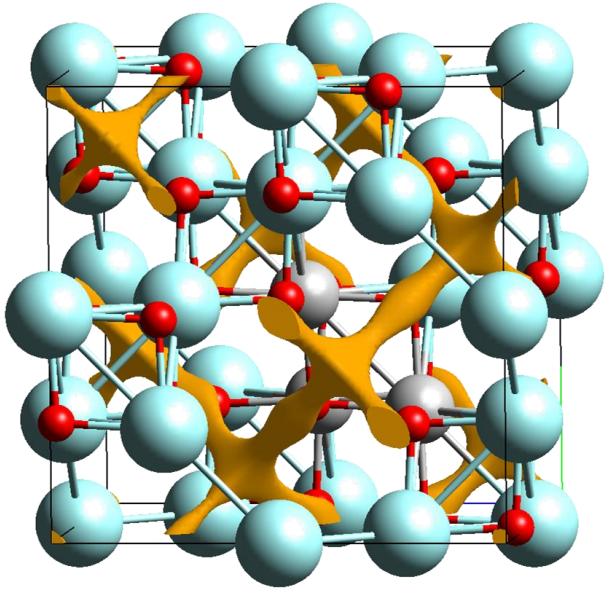
8*a* site: Li
32*e* site: O
16*d* site: 1/6 Li, 5/6 Ti

'densest framework'



ρ_{pro}(migration) = 0.0040 au

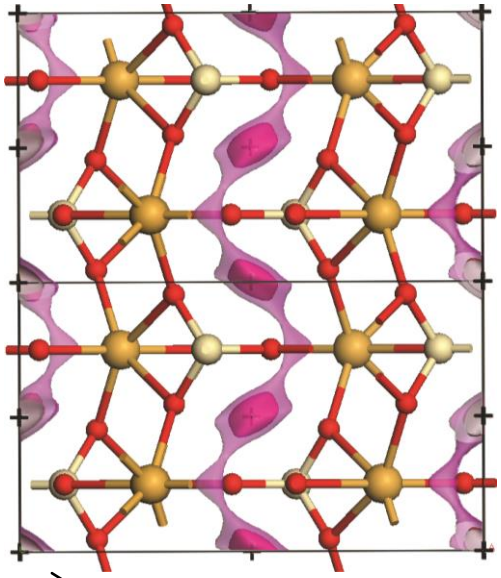
'actual stoichiometry'
(16d Li stationary)



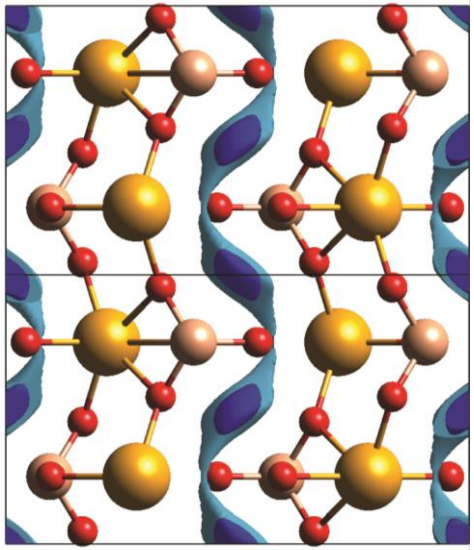
ρ_{pro}(migration) = 0.0040 au

COMPARISON WITH BOND VALENCE THEORY

$LiFePO_4$



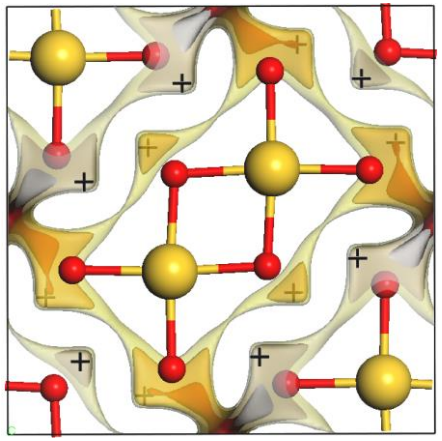
$E_{BV}(1)$ = 0.35 eV (dark pink)
$E_{BV}(2)$ = 0.64 eV (light pink)



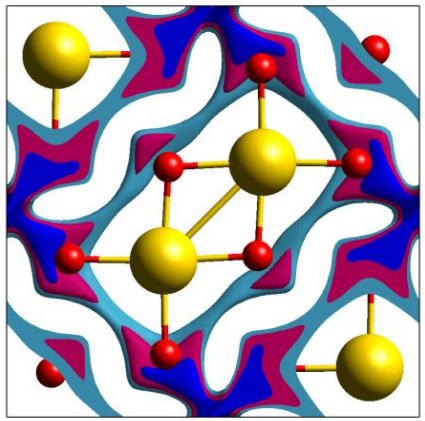
$\rho_{pro}(1)$ = 0.0021 au (dark blue)
$\rho_{pro}(2)$ = 0.0026 au (light blue)

Li_3AuO_3

$E_{BV}(1)$ = 0.50 eV
$E_{BV}(2)$ = 1.20 eV
$E_{BV}(3)$ = 1.50 eV



$\rho_{pro}(1)$ = 0.0019 au
$\rho_{pro}(2)$ = 0.0023 au
$\rho_{pro}(3)$ = 0.0027 au



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National University of Singapore

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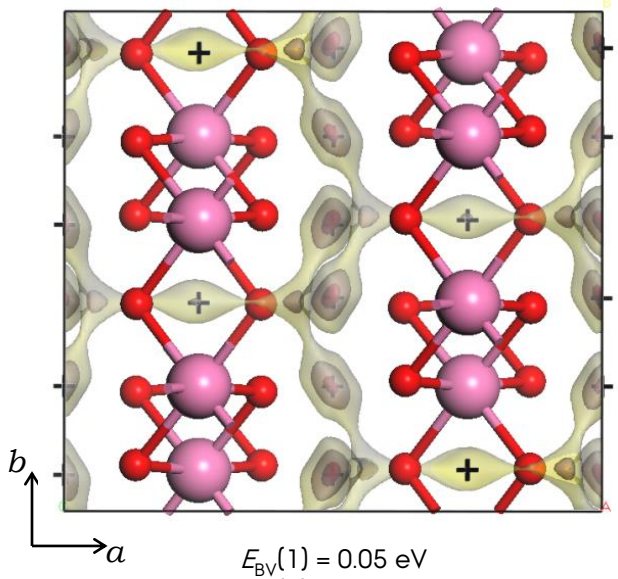
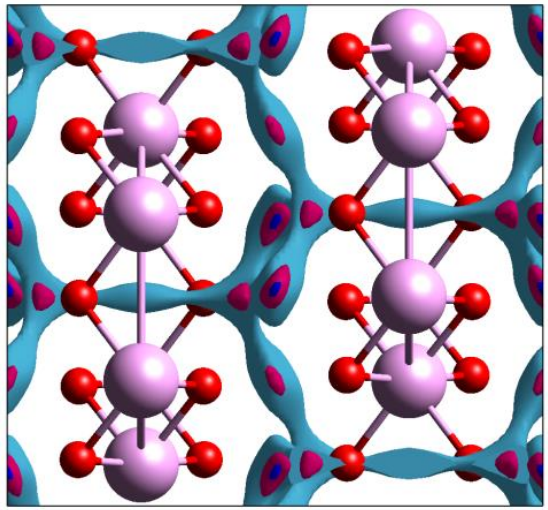
COMPARISON WITH BOND VALENCE THEORY

$Li_{1.8}SnO_3$



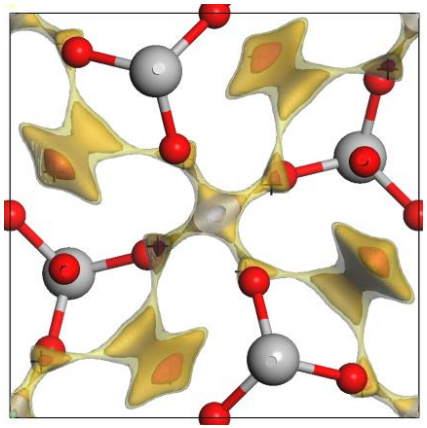
$E_{BV}(1) = 0.05$ eV
$E_{BV}(2) = 0.30$ eV
$E_{BV}(3) = 0.80$ eV



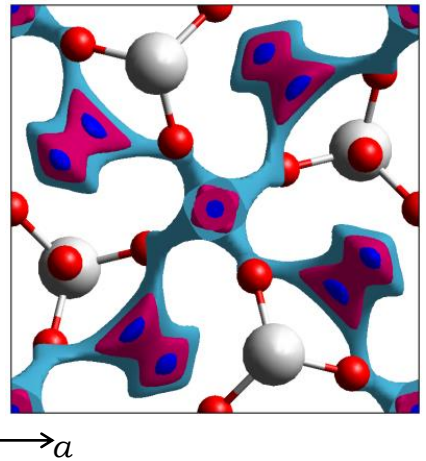
$\rho_{pro}(1) = 0.0016$ au
$\rho_{pro}(2) = 0.0018$ au
$\rho_{pro}(3) = 0.0025$ au

$Li_6Si_2O_7$

$E_{BV}(1) = 0.10$ eV
$E_{BV}(2) = 0.40$ eV
$E_{BV}(3) = 0.48$ eV



$\rho_{pro}(1) = 0.0013$ au
$\rho_{pro}(2) = 0.0016$ au
$\rho_{pro}(3) = 0.0020$ au



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- Prof. Mark Arthur Spackman
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- CMC/iNANO
- Danish National Research Fondation