ES18: Electronic Structure Workshop -- hosted by U. Penn

Perspectives on the Projector Augmented Wave Method (PAW)

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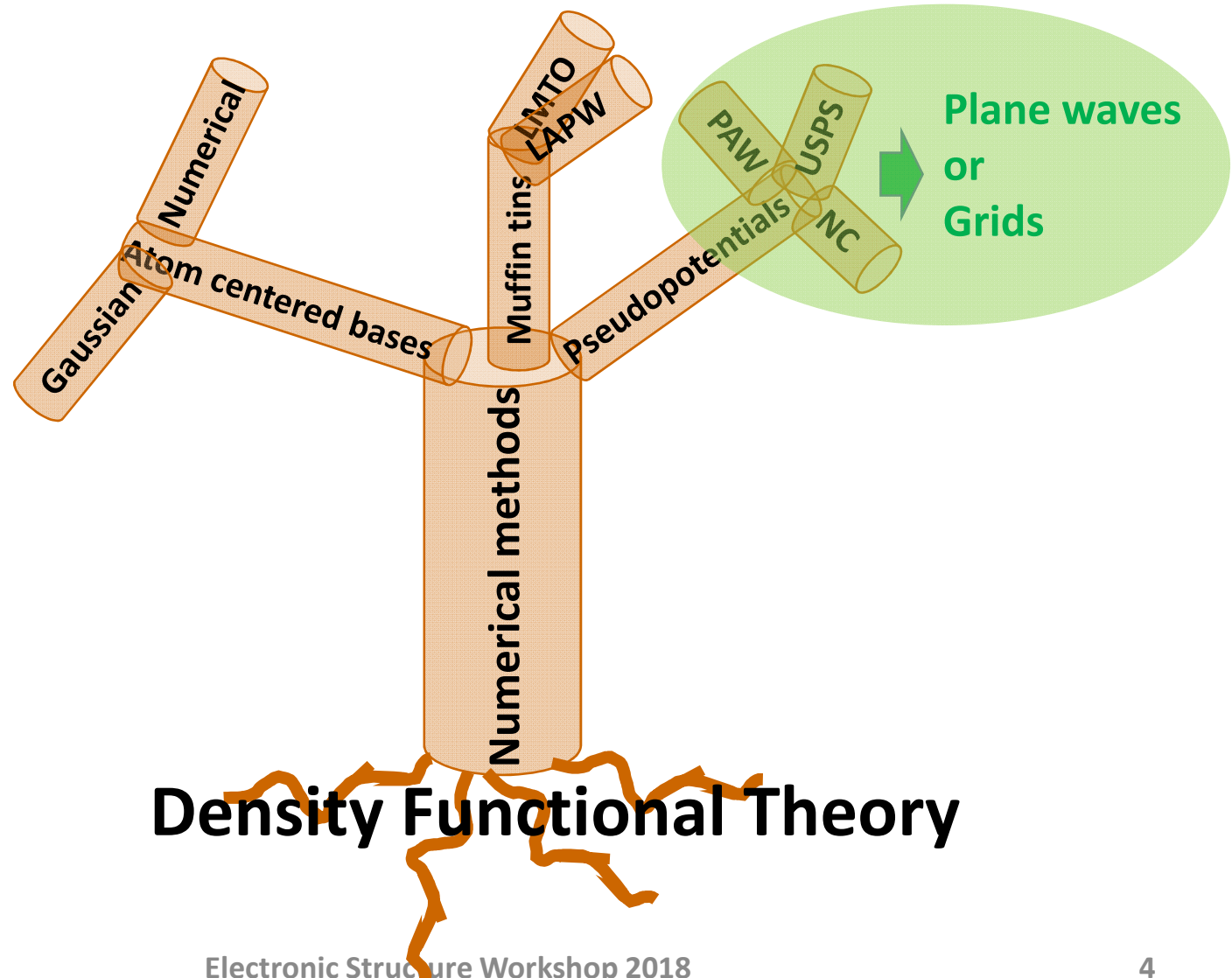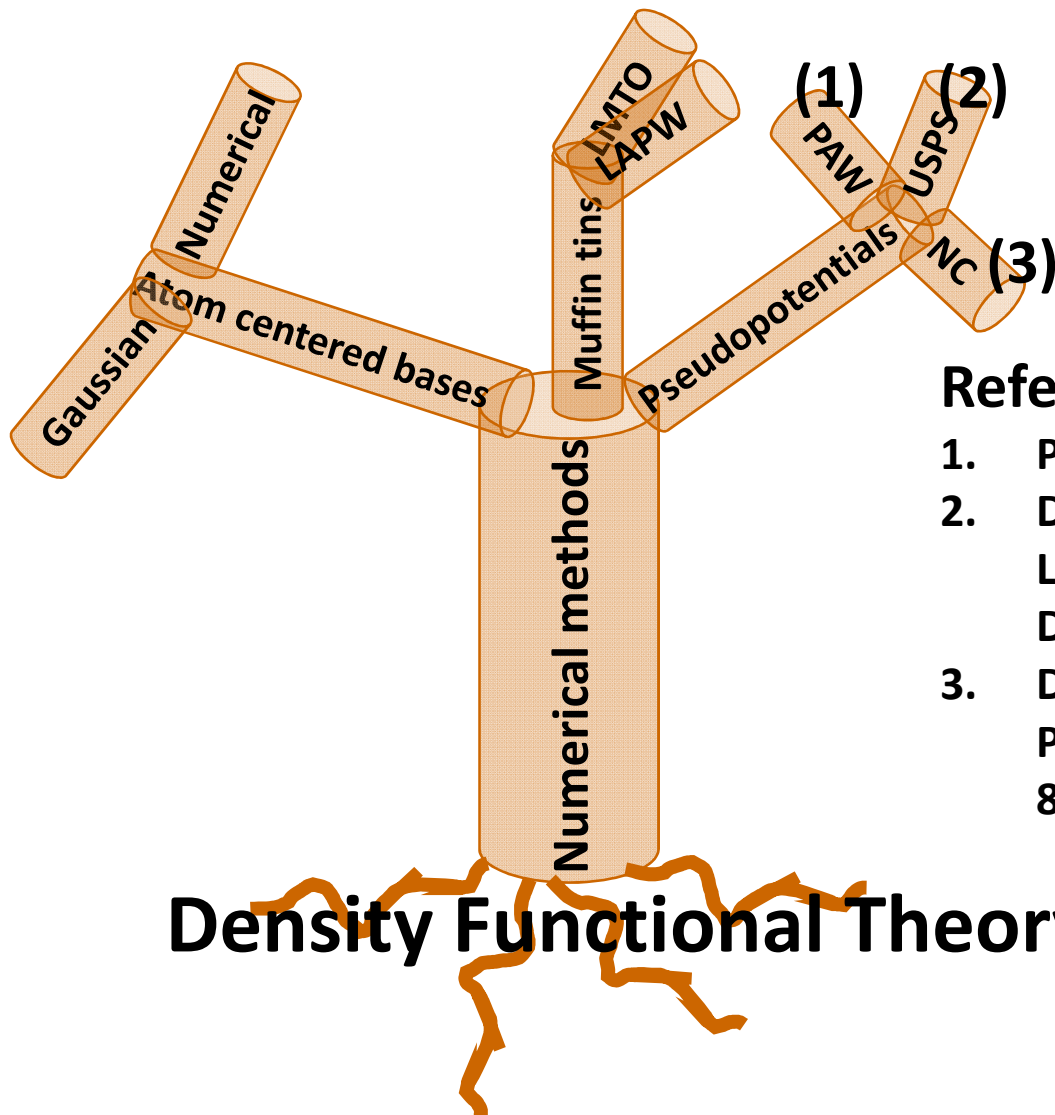
Acknowledgements:

Outline

- **Some history**
- **PAW vs NC and USPP**
- **PAW details**
- **PAW advice**
- **Example application -- the study of solid electrolytes**

input parameters → [quantum-espresso (http://www.quantum-espresso.org/), abinit (https://www.abinit.org/), VASP (https://www.vasp.at/), Qbox (http://qboxcode.org/), RMG (http://rmgdft.sourceforge.net/)] → useful results

Inside the box --

Density Functional Theory

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U N I V E R S I T Y

Numerical

Gaussian

Atom centered bases

Muffin tins

Numerical methods

LMTO

LAPW

PAW

USPS

NC

Pseudopotentials

(1) (2)

(3)

References:

1. P. E. Blöchl, PRB 50, 17953 (1994)
2. D. Vanderbilt, PRB 41, 7892 (1990); K. Laasonen, A. Pasquarello, R. Car, C. Lee, D. Vanderbilt, PRB 47, 10142 (1993)
3. D. R. Hamann, M. Schlüter, C. Chiang, PRL 43, 1494 (1979); D. R. Hamann, PRB 88, 085117 (2013)

Density Functional Theory

Basic ideas of the Projector Augmented Wave (PAW) method

Peter Blöchl,
Institute of Theoretical Physics
TU Clausthal, Germany

Blöch presented his ideas at ES93 --"PAW: an all-electron method for first-principles molecular dynamics"
Reference: P. E. Blöchl, PRB 50, 17953 (1994)

Features

- Operationally similar to other pseudopotential methods, particularly to the ultra-soft pseudopotential method of D. Vanderbilt; often run within frozen core approximation
- Can retrieve approximate ''all-electron'' wavefunctions from the results of the calculation; useful for NMR analysis for example
- May have additional accuracy controls particularly of the higher multipole Coulombic contributions.

Basic ideas of the Projector Augmented Wave (PAW) method

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- **Valence electron wavefunctions are approximated by the form**

$$\Psi_{n\mathbf{k}}(\mathbf{r}) \approx \tilde{\Psi}_{n\mathbf{k}}(\mathbf{r}) + \sum_{ab}\left(\varphi_b^a(\mathbf{r}-\mathbf{R}_a) - \tilde{\varphi}_b^a(\mathbf{r}-\mathbf{R}_a)\right)\left\langle \tilde{p}_b^a(\mathbf{r}-\mathbf{R}_a)\middle|\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r})\right\rangle$$

All-electron wavefunction

Pseudowavefunction, optimized in solving Kohn-Sham equations

Atom-centered functions:
All electron basis functions
Pseudo basis functions
Projector functions

$\left\{\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r})\right\}$: determined self-consistently within calculation

$\left\{\varphi_b^a(\mathbf{r}), \tilde{\varphi}_b^a(\mathbf{r}), \tilde{p}_b^a(\mathbf{r})\right\}$: part of pseudopotential construction; stored in PAW dataset

Basic ideas of the Projector Augmented Wave (PAW) method

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- **Evaluation of the total electronic energy:**
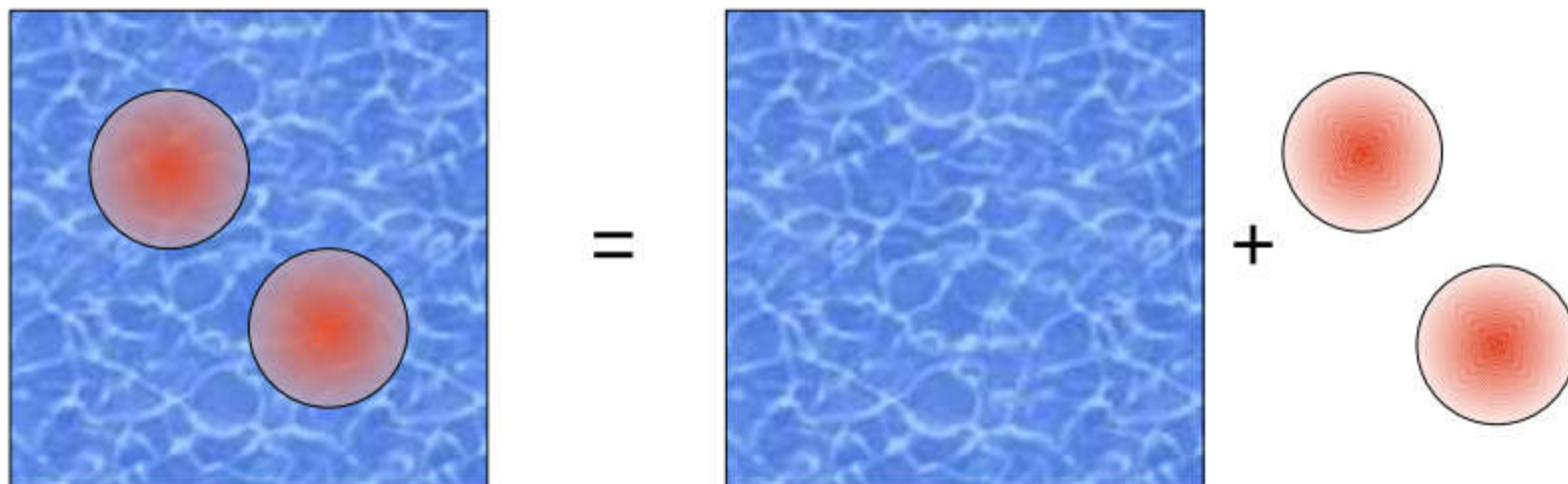
$$E_{\text{total}} \quad = \quad \tilde{E}_{\text{total}} \quad + \quad \sum_a \Delta E_a$$

Pseudoenergy (evaluated in plane wave basis or on regular grid)

One-center atomic contributions (evaluated within augmentation spheres)

Comment on one center energy contributions

- **Norm-conserving pseudopotential scheme using the Kleinman-Bylander method (PRL 48, 1425 (1982)):**

  The non-local pseudopotential contributions for site a :

  $$\Delta E_a = \sum_{n\mathbf{k},b} W_{n\mathbf{k}} \left\langle \tilde{\Psi}_{n\mathbf{k}} \middle| \tilde{\chi}_b^a \right\rangle \left\langle \tilde{\chi}_b^a \middle| \tilde{\Psi}_{n\mathbf{k}} \right\rangle, \text{ where } \tilde{\chi}_b^a(\mathbf{r} - \mathbf{R}^a) \text{ are}$$

  fixed functions depending on the non-local pseudopotentials and corresponding pseudobasis functions; $W_{n\mathbf{k}}$ are occupancy and sampling weights.

- **PAW and USPS :**

  $$\Delta E_a = \sum_{n\mathbf{k},bb'} W_{n\mathbf{k}} \left\langle \tilde{\Psi}_{n\mathbf{k}} \middle| \tilde{p}_b^a \right\rangle M_{bb'}^a \left\langle \tilde{p}_{b'}^a \middle| \tilde{\Psi}_{n\mathbf{k}} \right\rangle, \text{ where } \tilde{p}_b^a(\mathbf{r} - \mathbf{R}^a) \text{ are}$$

  projector functions, $M_{bb'}^a$ are matrix elements depending on all-electron and pseudobasis functions, and $W_{n\mathbf{k}}$ are occupancy and Brillouin zone sampling weights.

Comment on one center energy contributions
-- continued for PAW and USPS

$M^a_{bb'}$ matrix elements (different for USPS and PAW) are evaluated within the augmentation spheres. For example, the kinetic energy term:

$$K^a_{bb'} = \delta_{l_b l_{b'}} \delta_{m_b m_{b'}} \frac{\hbar^2}{2m} \left(\int_0^{r_c} dr \left(\frac{d\phi^a_b(r)}{dr} \frac{d\phi^a_{b'}(r)}{dr} - \frac{d\tilde{\phi}^a_b(r)}{dr} \frac{d\tilde{\phi}^a_{b'}(r)}{dr} \right) \right.$$

$$\left. + l_b(l_b + 1) \left(\int_0^{r_c} \frac{dr}{r^2} \left(\phi^a_b(r)\phi^a_{b'}(r) - \tilde{\phi}^a_b(r)\tilde{\phi}^a_{b'}(r) \right) \right) \right)$$

where $\varphi^a_b(\mathbf{r}) \equiv \dfrac{\phi^a_b(r)}{r} Y_{l_b m_b}(\hat{\mathbf{r}})$ and $\tilde{\varphi}^a_b(\mathbf{r}) \equiv \dfrac{\tilde{\phi}^a_b(r)}{r} Y_{l_b m_b}(\hat{\mathbf{r}})$

Note that for USPS, the operator $Q^a_{bb'}(r) \equiv \left(\phi^a_b(r)\phi^a_{b'}(r) - \tilde{\phi}^a_b(r)\tilde{\phi}^a_{b'}(r) \right)$

is pseudized, while for PAW it is evaluated within matrix elements and "compensation charges" are added. In both cases, multipole moments are conserved.

Summary of properties of norm-conserving (NC), ultra-soft-pseudopotential (USPS) and projector augmented wave (PAW) methods

	NC	USPS	PAW
Conservation of charge	✓	✓	✓
Multipole moments in Hartree interaction		✓	✓
Retrieve all-electron wavefunction			✓

Some details – use of "compensation charge"

PAW approximation to valence all-electron wave function

$$\Psi_{n\mathbf{k}}(\mathbf{r}) \approx \tilde{\Psi}_{n\mathbf{k}}(\mathbf{r}) + \sum_{ab}\left(\varphi_b^a(\mathbf{r}-\mathbf{R}_a) - \tilde{\varphi}_b^a(\mathbf{r}-\mathbf{R}_a)\right)\left\langle \tilde{p}_b^a(\mathbf{r}-\mathbf{R}_a)\middle|\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r})\right\rangle$$

PAW approximation to all-electron density

$$n_{\text{valence}}(\mathbf{r}) \approx \sum_{n\mathbf{k}} W_{n\mathbf{k}}\left|\Psi_{n\mathbf{k}}(\mathbf{r})\right|^2$$

$$\approx \sum_{n\mathbf{k}} W_{n\mathbf{k}}\left|\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r})\right|^2$$

$$+ \sum_{n\mathbf{k}} W_{n\mathbf{k}}\sum_{a,bb'}\left\langle\tilde{\Psi}_{n\mathbf{k}}\middle|\tilde{p}_b^a\right\rangle\left\langle\tilde{p}_{b'}^a\middle|\tilde{\Psi}_{n\mathbf{k}}\right\rangle\left(\varphi_b^a(\mathbf{r}-\mathbf{R}_a)\varphi_{b'}^a(\mathbf{r}-\mathbf{R}_a) - \tilde{\varphi}_b^a(\mathbf{r}-\mathbf{R}_a)\tilde{\varphi}_{b'}^a(\mathbf{r}-\mathbf{R}_a)\right)$$

$$\equiv \sum_{n\mathbf{k}} W_{n\mathbf{k}}\left(\left|\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r})\right|^2 + \sum_{a,bb'}\left\langle\tilde{\Psi}_{n\mathbf{k}}\middle|\tilde{p}_b^a\right\rangle\left\langle\tilde{p}_{b'}^a\middle|\tilde{\Psi}_{n\mathbf{k}}\right\rangle Q_{bb'}^a(\mathbf{r}-\mathbf{R}_a)\right)$$

$$\equiv \tilde{n}(\mathbf{r}) + \sum_a\left(n^a(\mathbf{r}-\mathbf{R}_a) - \tilde{n}^a(\mathbf{r}-\mathbf{R}_a)\right)$$

$$= \tilde{n}(\mathbf{r}) + \textcolor{red}{\sum_a \hat{n}^a(\mathbf{r}-\mathbf{R}^a)} + \sum_a\left(n^a(\mathbf{r}-\mathbf{R}_a) - \tilde{n}^a(\mathbf{r}-\mathbf{R}_a) \textcolor{red}{- \hat{n}^a(\mathbf{r}-\mathbf{R}^a)}\right)$$

Some details – use of "compensation charge" -- continued

Compensation charge is designed to have the same multipole moments of one-center charge differences:

$$\int\limits_{r \le r_c^a} d^3r \; r^L Y_{LM}(\hat{\mathbf{r}}) \hat{n}^a(\mathbf{r}) = \int\limits_{r \le r_c^a} d^3r \; r^L Y_{LM}(\hat{\mathbf{r}}) \left(n^a(\mathbf{r}) - \tilde{n}^a(\mathbf{r}) \right)$$

Typical shape of compensation charge for L=0 component --

$L = 0$

r_c
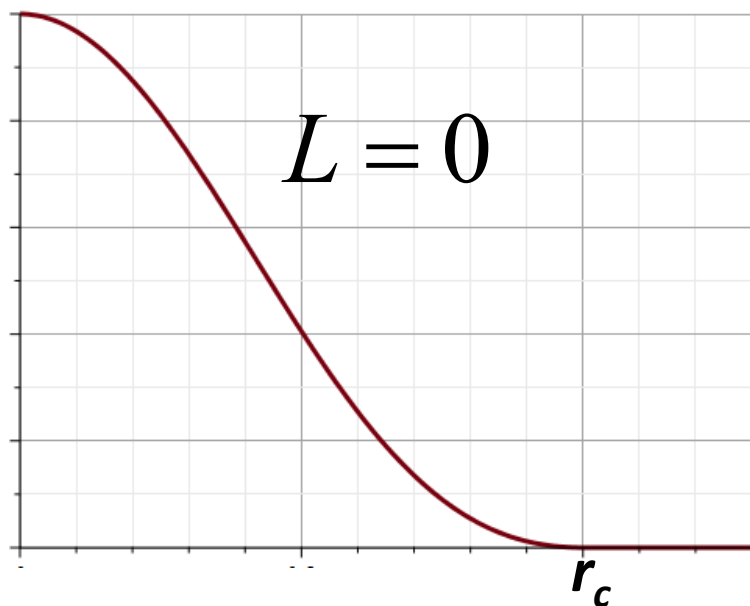
Some details – use of "compensation charge"
-- continued

The inclusion of the "compensation" charge ensures

1. Hartree energy of smooth charge density represents correct charge

2. Hartree energy contributions of one-center charge is confined within augmentation sphere:

$$\int_{r \leq r_c^a} d^3r' \frac{n^a(\mathbf{r}) - \tilde{n}^a(\mathbf{r}) - \hat{n}^a(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} = \begin{cases} V_{\text{Hartree}}^a(\mathbf{r}) & \text{for } r \leq r_c^a \\ 0 & \text{for } r > r_c^a \end{cases}$$

Some details – form of exchange-correlation contributions

For $\quad E_{xc}[n(\mathbf{r})] \equiv \int d^3r \; K_{xc}(n(\mathbf{r})):$

non-linear core correction (S. G. Louie et al. PRB 26, 1738 (1982))

Smooth contribution: $\quad \tilde{E}_{xc} = E_{xc}[\tilde{n}(\mathbf{r}) + \tilde{n}_{\text{core}}(\mathbf{r})]$

One-center contributions: $\quad E_{xc}^a - \tilde{E}_{xc}^a = E_{xc}[n^a(\mathbf{r}) + n^a{}_{\text{core}}(\mathbf{r})] - E_{xc}[\tilde{n}^a(\mathbf{r}) + \tilde{n}^a_{\text{core}}(\mathbf{r})]$

Note that VASP and Quantum-Espresso use

$E_{xc}[\tilde{n}(\mathbf{r}) + \tilde{n}_{\text{core}}(\mathbf{r}) + \hat{n}(\mathbf{r})]$

and $\quad E_{xc}[\tilde{n}^a(\mathbf{r}) + \tilde{n}^a_{\text{core}}(\mathbf{r}) + \hat{n}^a(\mathbf{r})]$

which can cause trouble occasionally.

Measure of accuracy

Binding energy curve for CsBr
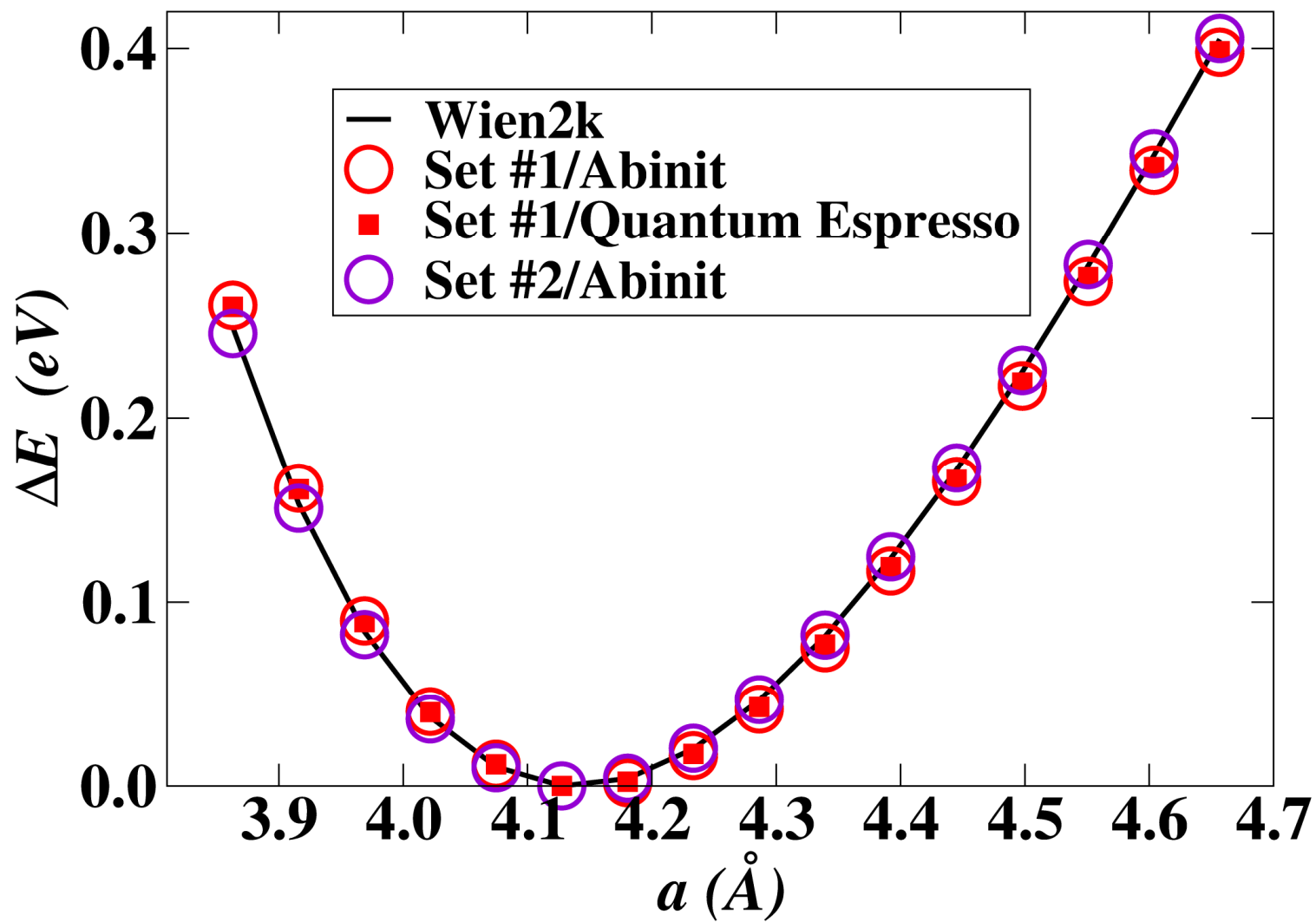
Recipes for constructing projector and basis functions

$$\varphi_b^a(\mathbf{r}) = \frac{\varphi_b^a(r)}{r} Y_{l_b m_b}(\hat{\mathbf{r}}) \qquad \tilde{\varphi}_b^a(\mathbf{r}) = \frac{\tilde{\varphi}_b^a(r)}{r} Y_{l_b m_b}(\hat{\mathbf{r}}) \qquad \tilde{p}_b^a(\mathbf{r}) = \frac{\tilde{p}_b^a(r)}{r} Y_{l_b m_b}(\hat{\mathbf{r}})$$

Constraints:
$$\tilde{\varphi}_b^a(r) = \varphi_b^a(r) \quad \text{for } r \geq r_c^a$$

$$\tilde{p}_b^a(r) = 0 \qquad \text{for } r \geq r_c^a$$

$$\langle \tilde{p}_b^a | \tilde{\varphi}_{b'}^a \rangle = \delta_{bb'}$$

Peter Blöchl's scheme (set #1)

Choose projectors $\tilde{p}_b^a(r)$*

$\Rightarrow$ Derive $\tilde{\varphi}_b^a(r)$

*Typically Bessel-like function with zero value and derivative at r_c^a

David Vanderbilt's scheme (set #2)

Choose pseudo bases $\tilde{\varphi}_b^a(r)$*

$\Rightarrow$ Derive $\tilde{p}_b^a(r)$

*Polynomial or Bessel function form following RRKJ, PRB 41, 1227 (1990)

Example projector and basis functions

Br *4s* orbital
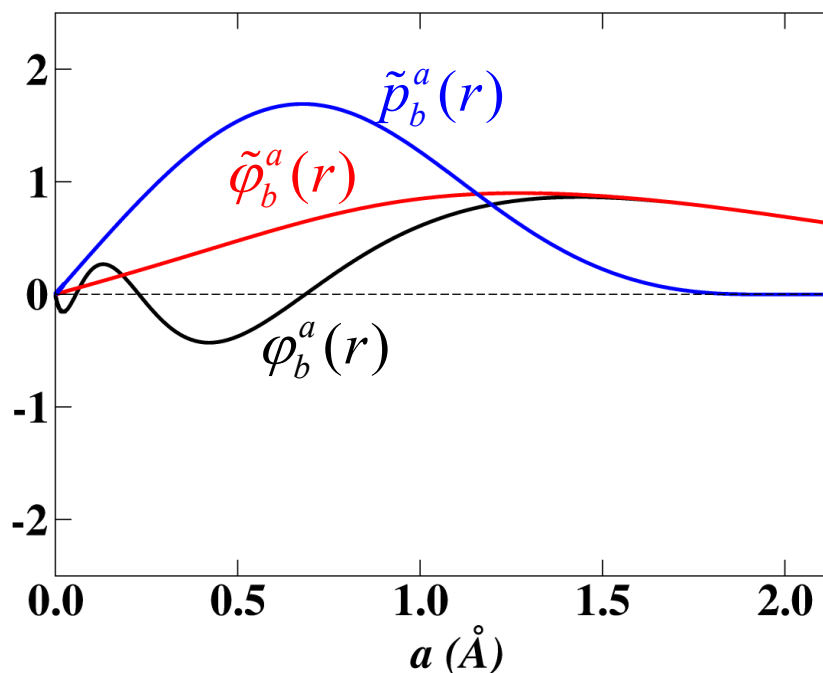
From set #1
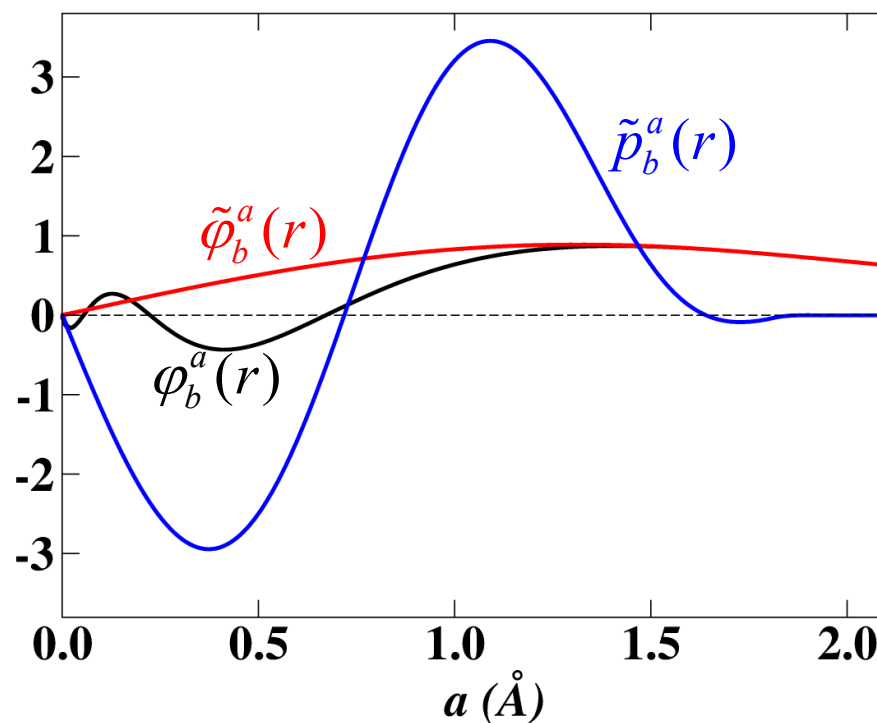
From set #2

Set of basis and projector functions for set #1

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Cs

Br
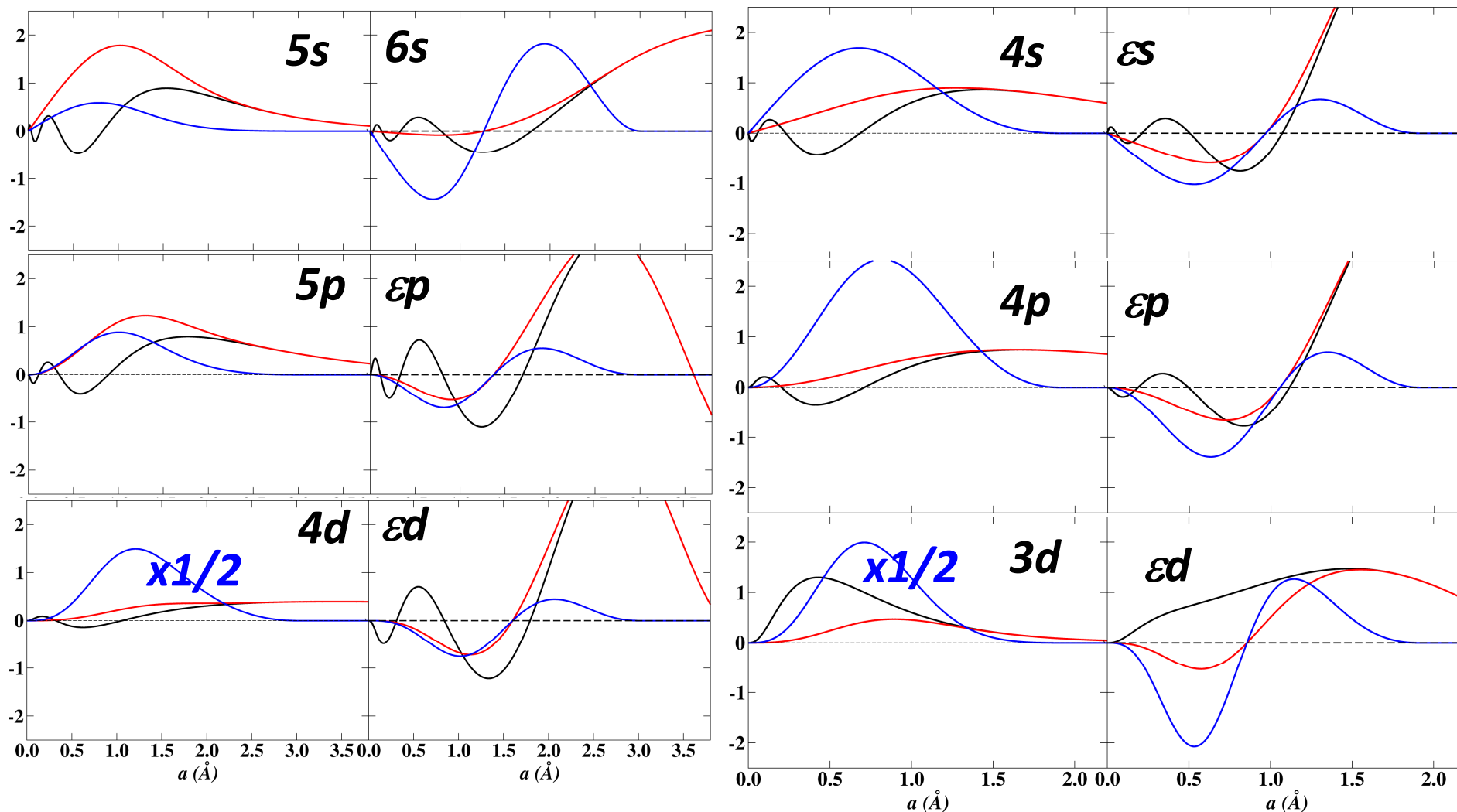
Efforts to use machine learning methods to optimize PAW datasets

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Automated generation of highly accurate, efficient and transferable pseudopotentials

R.A. Hansel [a], C.N. Brock [a], B.C. Paikoff [b], A.R. Tackett [c], D.G. Walker [b,*]

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[c] Department of Astronomy and Physics, Vanderbilt University, United States
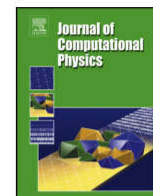
Evolutionary optimization of PAW data-sets for accurate high pressure simulations

Kanchan Sarkar [a,*], Mehmet Topsakal [a], N.A.W. Holzwarth [b],
Renata M. Wentzcovitch [a,c]

[a] Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA
[b] Department of Physics, Wake Forest University, Winston-Salem, NC 27109, USA
[c] Minnesota Supercomputing Institute for Digital Technology and Advanced Computations, University of Minnesota, Minneapolis, MN 55455, USA

General advice about generating PAW datasets

- ATOMPAW code* available at http://pwpaw.wfu.edu
- Develop and test atomic datasets for the full scope of your project ➔ determines r_c^a .
- Determine local pseudopotential from self-consistent all-electron potential
- Determine basis functions, with or without semicore states; usually 2 sets of basis functions and projectors for each l channel.
- Test binding energy curves for a few binary compounds related to your project.
- Check plane wave (or grid spacing convergence of your data sets before starting production runs.

*With major modification by Marc Torrent and other Abinit developers.

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Simulations of Idealized Solid Electrolytes

Theoretical battery

$$V = IR$$
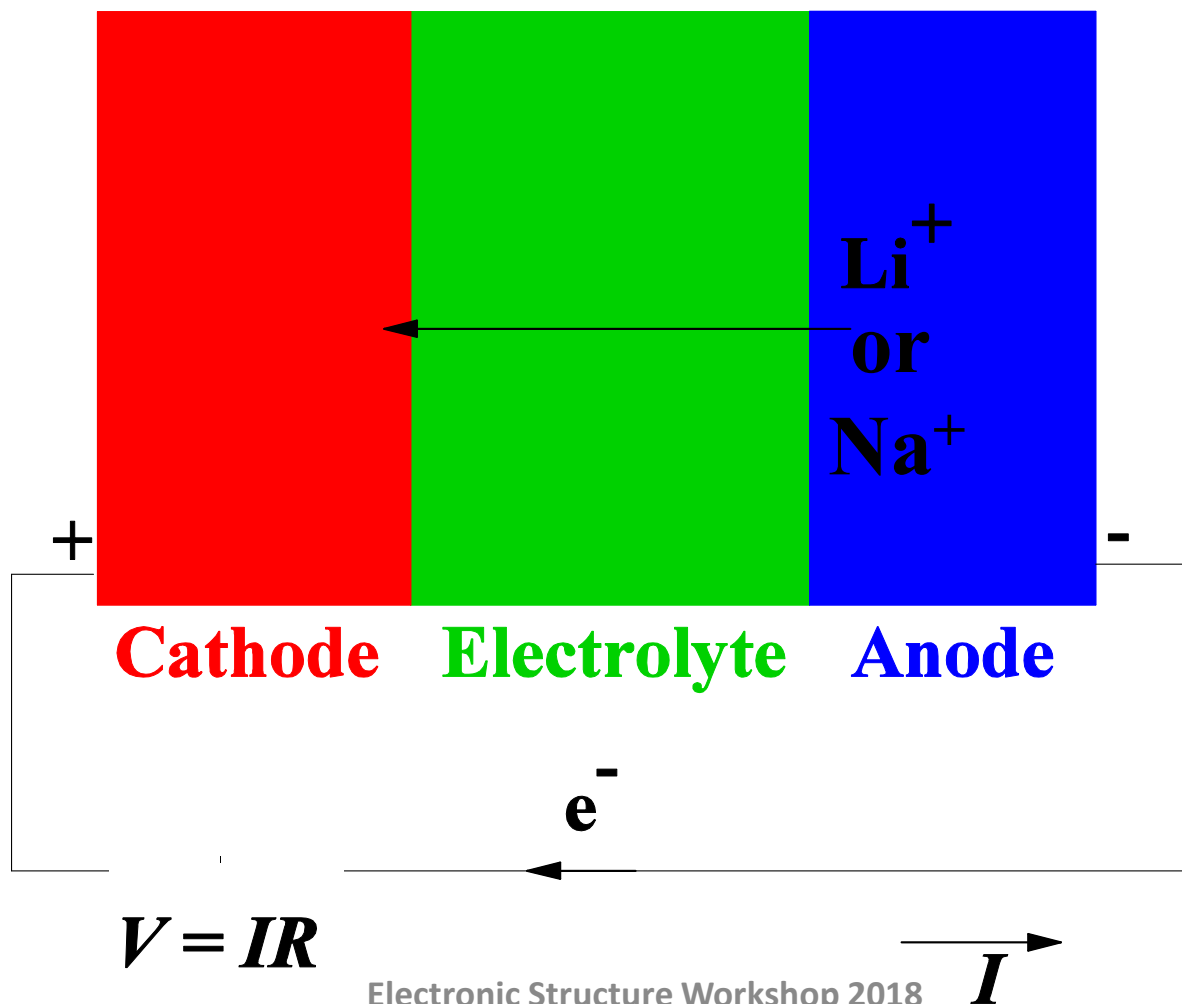
What can first principles modeling bring to the development of all solid state batteries?

- **Examine structures and stabilities of potential ionic conductors**
- **Examine mechanisms and model efficiencies for ionic conduction**
- **Model ideal interfaces between electrolytes and electrodes**

From Oak Ridge National Laboratory:

Solid Electrolyte: the Key for High-Voltage Lithium Batteries

Juchuan Li,* Cheng Ma, Miaofang Chi, Chengdu Liang, and Nancy J. Dudney*

Advantages	Disadvantages
➢ Compatible and stable with high voltage cathodes and with Li metal anodes	➢ Relatively low ionic conductivity (Compensated with the use of less electrolyte?) ➢ Lower total capacity

Demonstrated for $LiNi_{0.5}Mn_{1.5}O_4$/LiPON/Li

➢ 10^{-6} m LiPON electrolyte layer achieved adequate conductivity

➢ 10,000 cycles* with 90% capacity retention

*1 cycle per day for 27 years

Motivation: Paper by N. Kamaya, *et. al* in **Nature Materials 10**, 682-686 (2011)
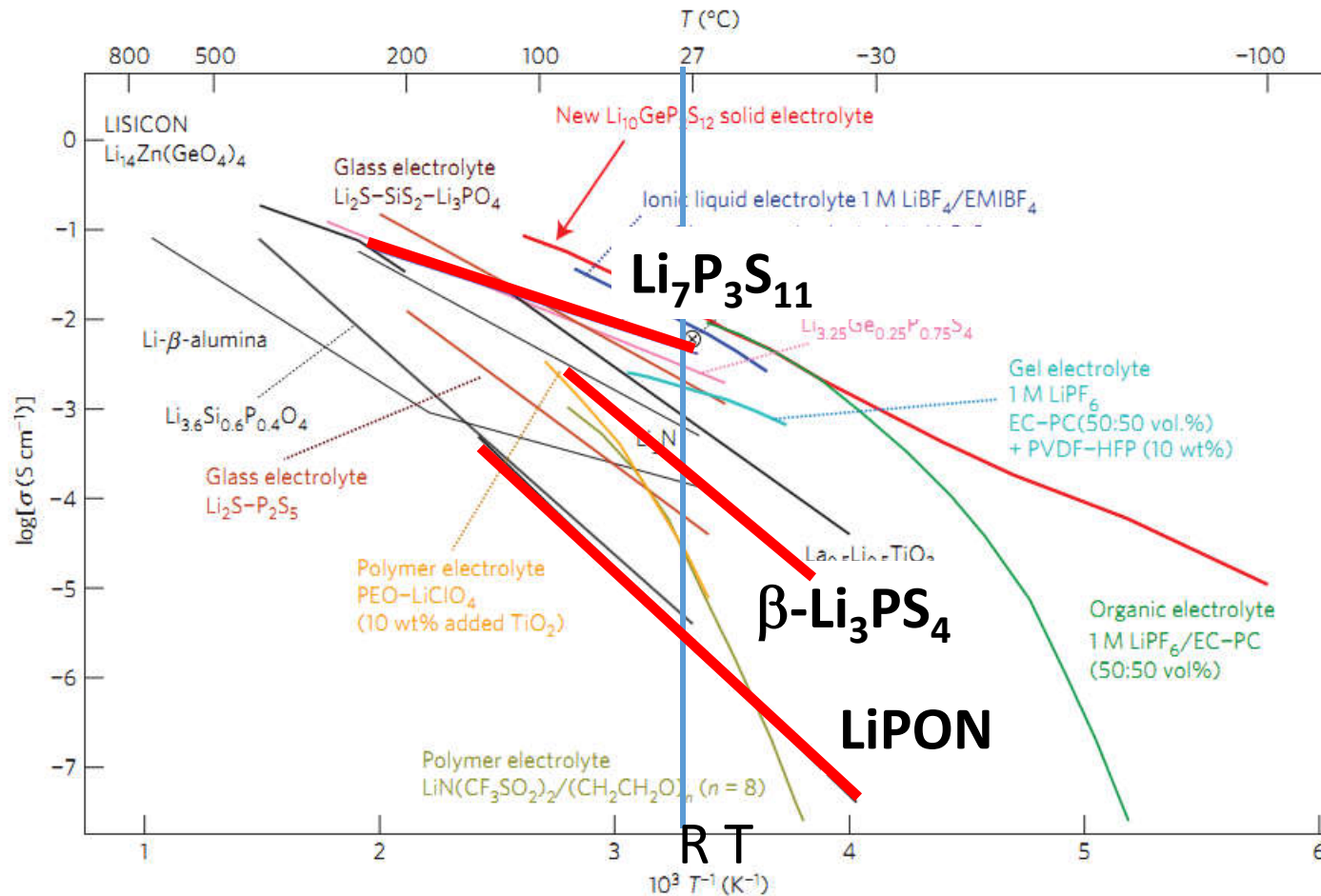
Solid electrolyte families investigated in this study:

$Li_xPO_yN_z$

Li_xPS_y

Li

Li

Li_3N Li_3P

Li_2O

Li_3P

Li_2S

Li_7PN_4

Li_7PS_6

$Li_{14}P_2O_3N_6$

Li_3PS_4

$Li_4P_2S_6$ $Li_7P_3S_{11}$

$LiPN_2$

Li_3PO_4

$Li_4P_2S_7$

Li_2PO_2N

$Li_4P_2O_7$

LiP_4N_7

$Li_xP_{(2y-x)/5}S_y$

$LiPO_3$

N

P

S

P_3N_5

P_2O_5

O

P
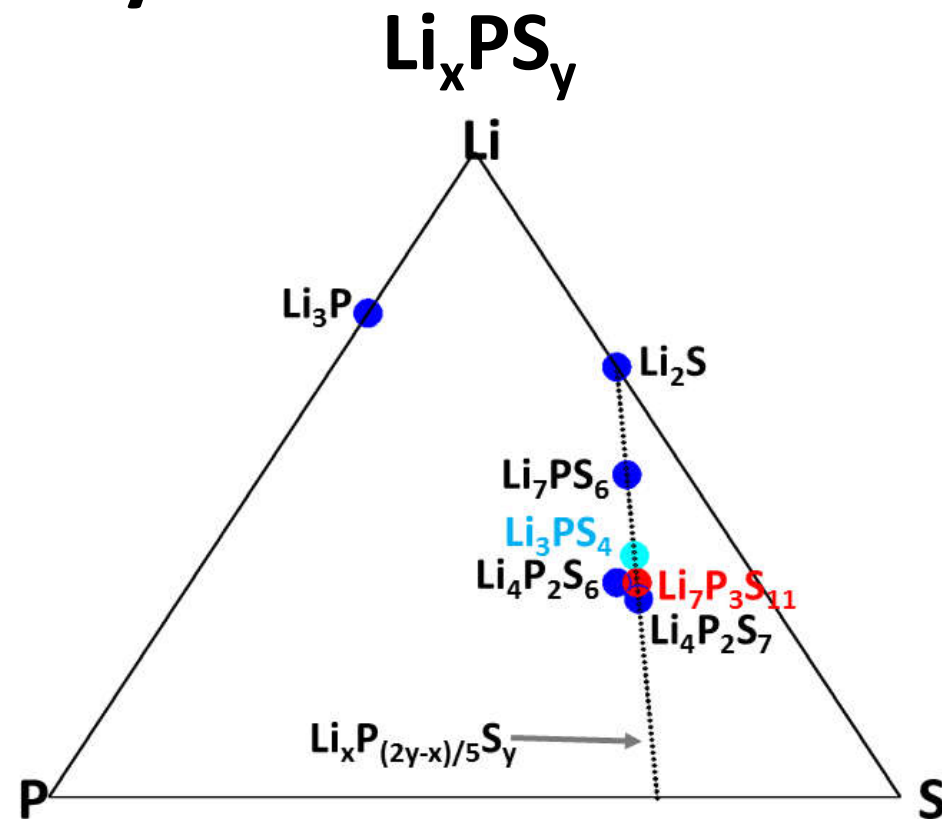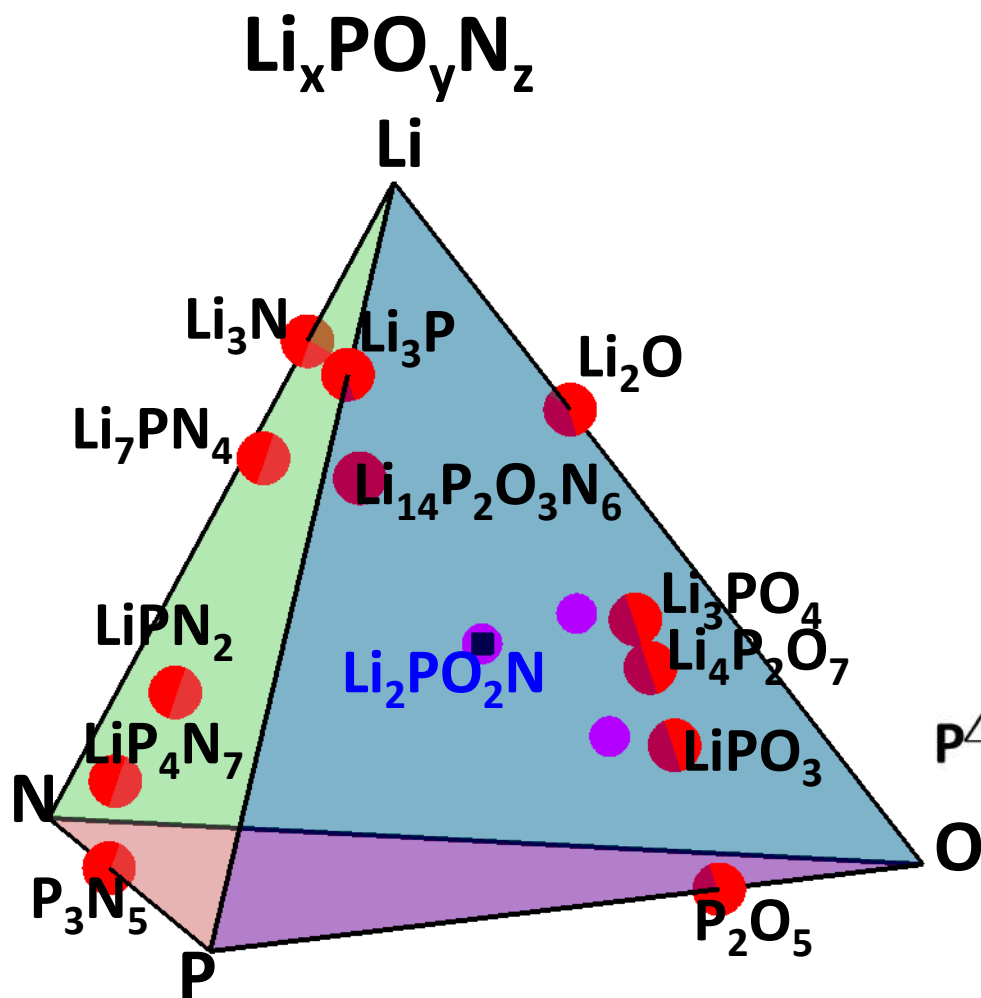
+ a few related materials such as Li_4SnS_4, $Na_4P_2S_6$, Na_3SbS_4

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Li$_3$PO$_4$ crystals

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γ-Li$_3$PO$_4$

Key

β-Li$_3$PO$_4$

- Li
- N
- O
- P
- S
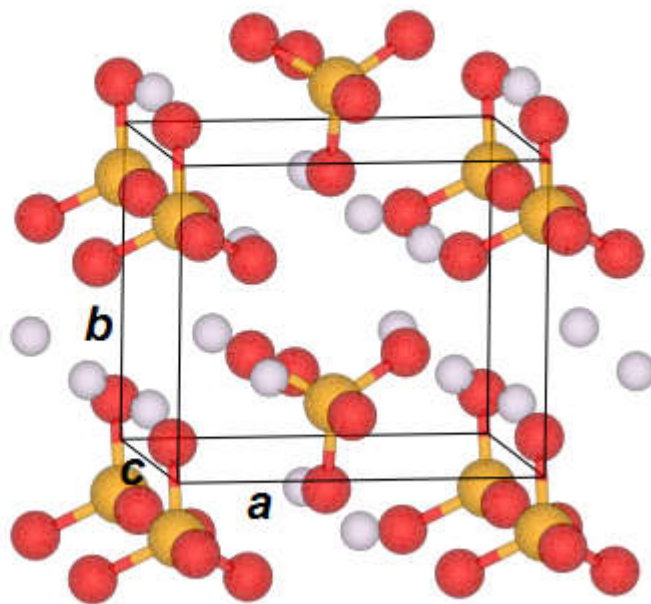
(Pmn2$_1$)
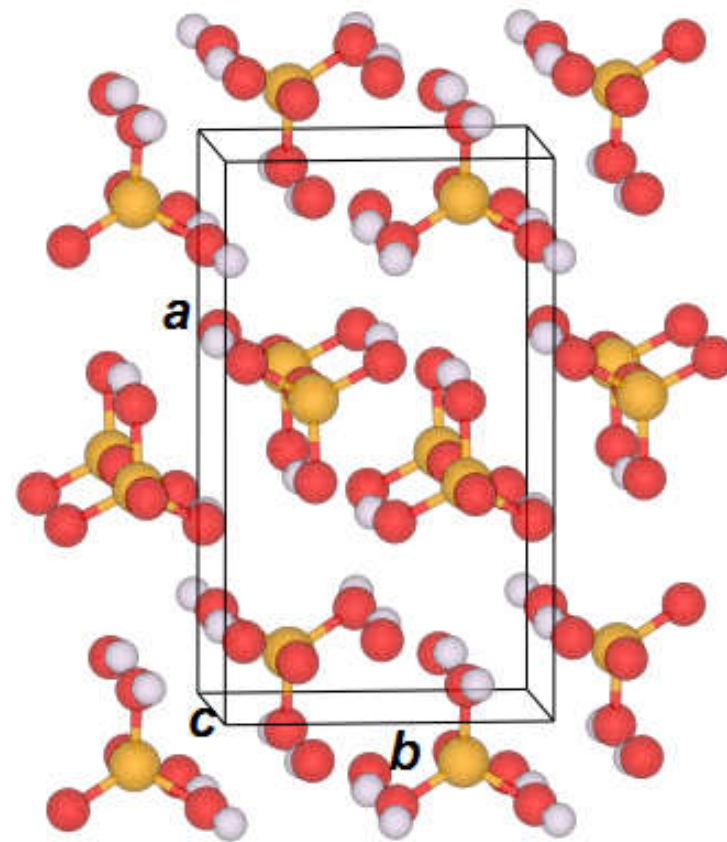
(Pnma)

Validation of calculations

Raman spectra – Experiment & Calculation

γ-Li$_3$PO$_4$

β-Li$_3$PO$_4$
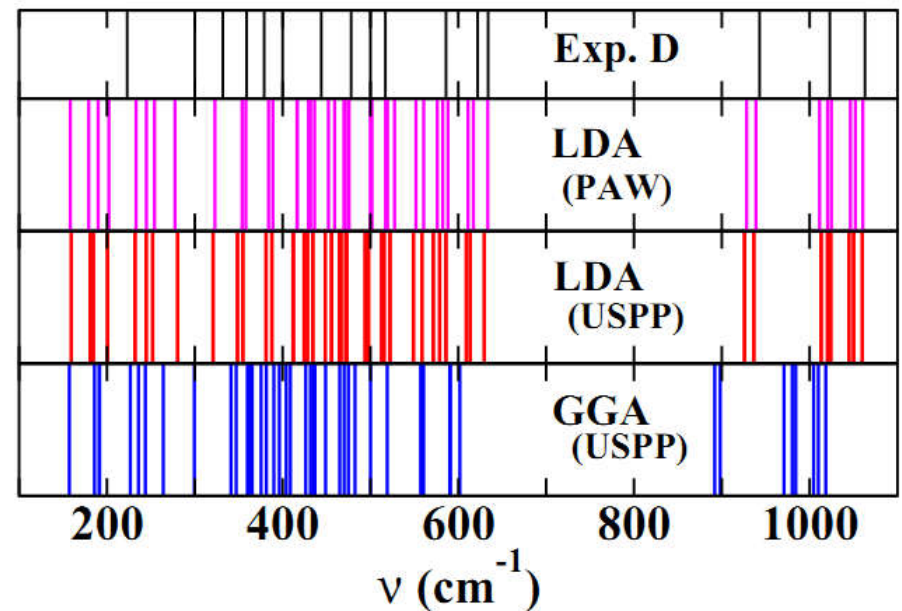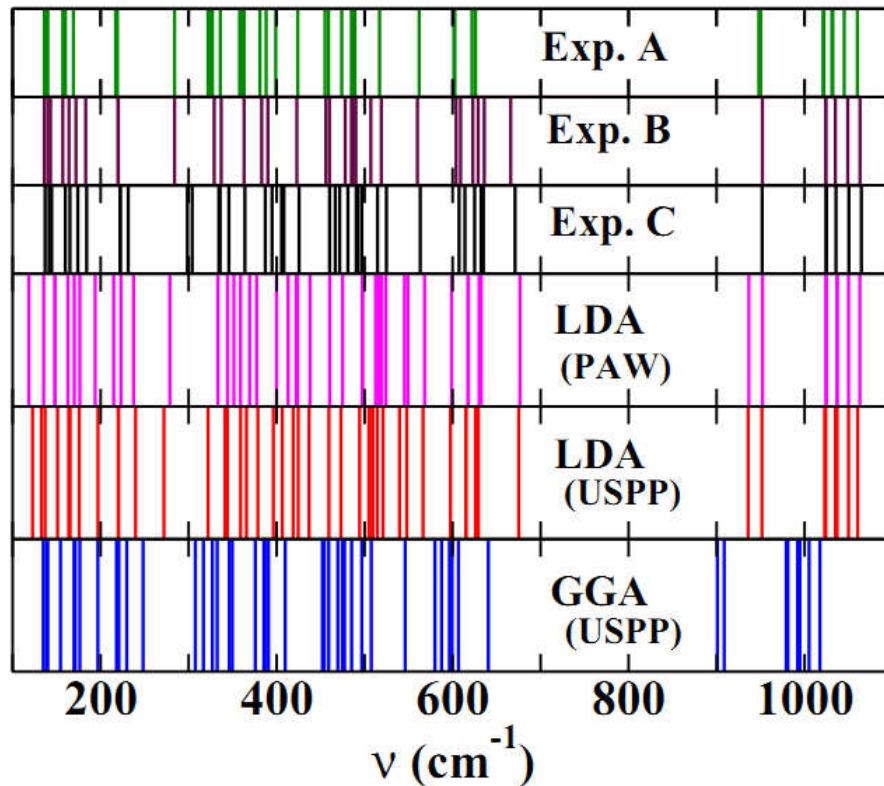
A: B. N. Mavrin et al, J. Exp. Theor. Phys. **96**,53 (2003); B: F. Harbach and F. Fischer, Phys. Status Solidi B **66**, 237 (1974) – room temp. C: Ref. B at liquid nitrogen temp.; D: L. Popović et al, J. Raman Spectrosc. **34**,77 (2003).

Heats of formation – Experiment & Calculation

Table 1. Calculated heats of formation for Li phosphates, phospho-nitrides, related materials. The structural designation uses the the notation defined in the international table of Crystallography[85] based on structural information reported in the International Crystal Structure Database.[86] The heats of formation ΔH (eV/FU) are given in units of eV per formula unit. When available from Ref. [31] and [32] experiment values are indicated in parentheses. Those indicated with "*" were used fitting the O and N reference energies as explained in the text.

Material	Structure	ΔH (eV/FU)
β-Li_3PO_4	$Pmn2_1$ (#31)	-21.23
γ-Li_3PO_4	$Pnma$ (#62)	-21.20 (-21.72*)
γ-Li_3PS_4	$Pmn2_1$ (#31)	- 8.37
β-Li_3PS_4	$Pnma$ (#62)	- 8.28
$Li_4P_2O_6$	$P\bar{3}1m$ (#162)	-29.72
$Li_4P_2O_7$	$P\bar{1}$ (#2)	-33.97
$Li_5P_2O_6N$	$P\bar{1}$ (#2)	-33.18
$Li_4P_2S_6$	$P\bar{3}1m$ (#162)	-12.42
$Li_4P_2S_7$	$P\bar{1}$ (#2)	-11.59
$Li_7P_3O_{11}$	$P\bar{1}$ (#2)	-54.84
$Li_7P_3S_{11}$	$P\bar{1}$ (#2)	-20.01
$LiPO_3$	$P2/c$ (#13)	-12.75
$LiPN_2$	$I\bar{4}2d$ (#122)	- 3.65
s1-Li_2PO_2N	$Pbcm$ (#57)	-12.35
SD-Li_2PO_2N	$Cmc2_1$ (#36)	-12.47
SD-Li_2PS_2N	$Cmc2_1$ (#36)	- 5.80

Material	Structure	ΔH (eV/FU)
N_2O_5	$P6_3/mmc$ (#194)	- 0.94 (- 0.45*)
P_3N_5	$C2/c$ (#15)	- 3.02 (- 3.32*)
h-P_2O_5	$R3c$ (#161)	-15.45 (-15.53*)
o-P_2O_5	$Fdd2$ (#43)	-15.78
P_2S_5	$P\bar{1}$ (#2)	- 1.93
P_4S_3	$Pnma$ (#62)	- 2.45 (- 2.33)
SO_3	$Pna2_1$ (#33)	- 4.84 (- 4.71*)
Li_3N	$P6/mmm$ (#191)	- 1.60 (- 1.71*)
Li_2O	$Fm\bar{3}m$ (#225)	- 6.10 (- 6.20*)
Li_2O_2	$P6_3/mmc$ (#194)	- 6.35 (- 6.57*)
Li_3P	$P6_3/mmc$ (#194)	- 3.47
Li_2S	$Fm\bar{3}m$ (#225)	- 4.30 (- 4.57)
Li_2S_2	$P6_3/mmc$ (#194)	- 4.09
$LiNO_3$	$R\bar{3}c$ (#167)	- 5.37 (- 5.01*)
Li_2SO_4	$P2_1/c$ (#14)	-14.63 (-14.89*)

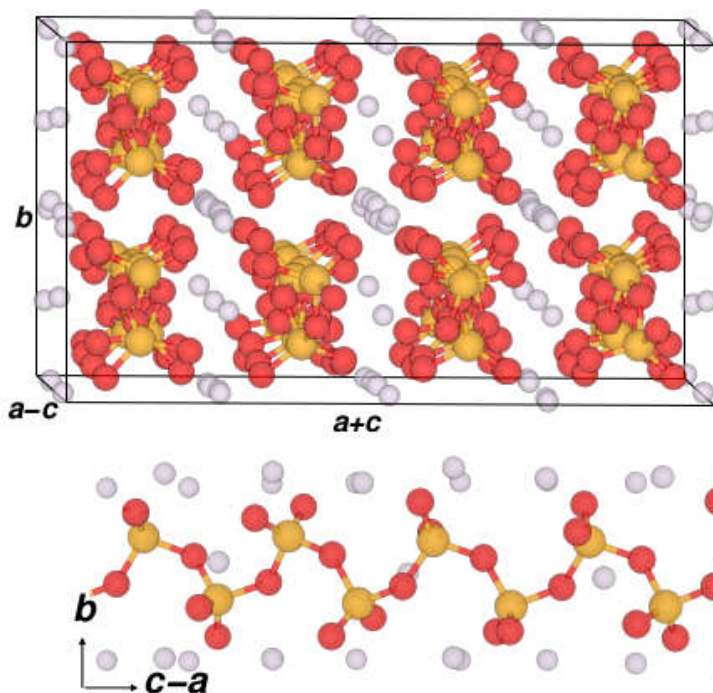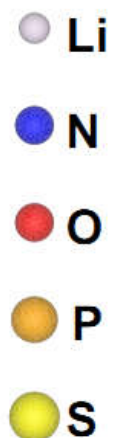# Systematic study of LiPON materials – $Li_xPO_yN_z$ – (Yaojun A. Du and N. A. W. Holzwarth, Phys. Rev. B 81, 184106 (2010))

Li

Li_3N Li_3P

Li_2O

Li_7PN_4

$Li_{14}P_2O_3N_6$

Typical composition of amorphous LiPON films

$LiPN_2$

Li_3PO_4

Li_2PO_2N $Li_4P_2O_7$

LiP_4N_7

N

$LiPO_3$

P_3N_5

O

P P_2O_5
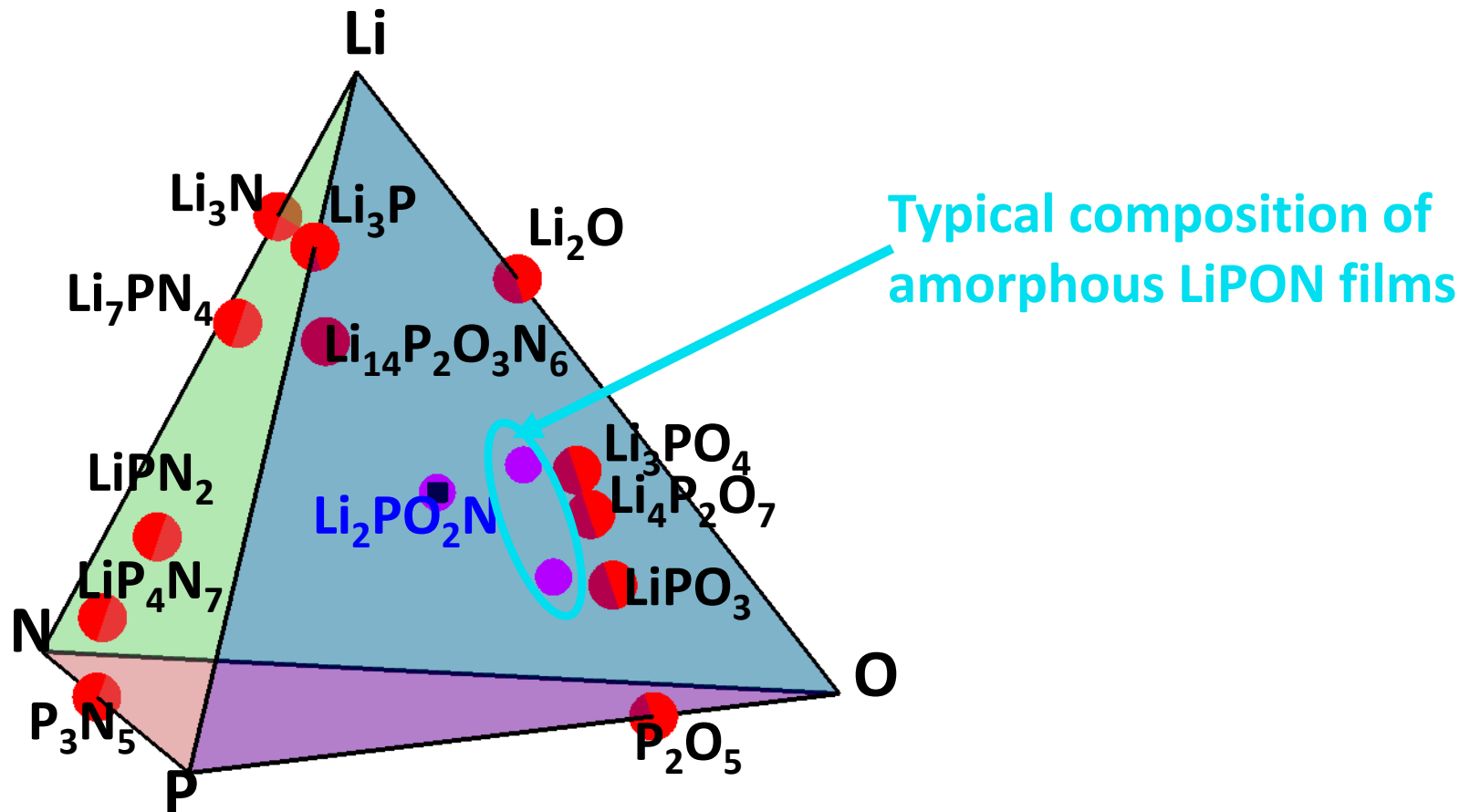
**Experimentally
known structure**

**Computationally
predicted structure**
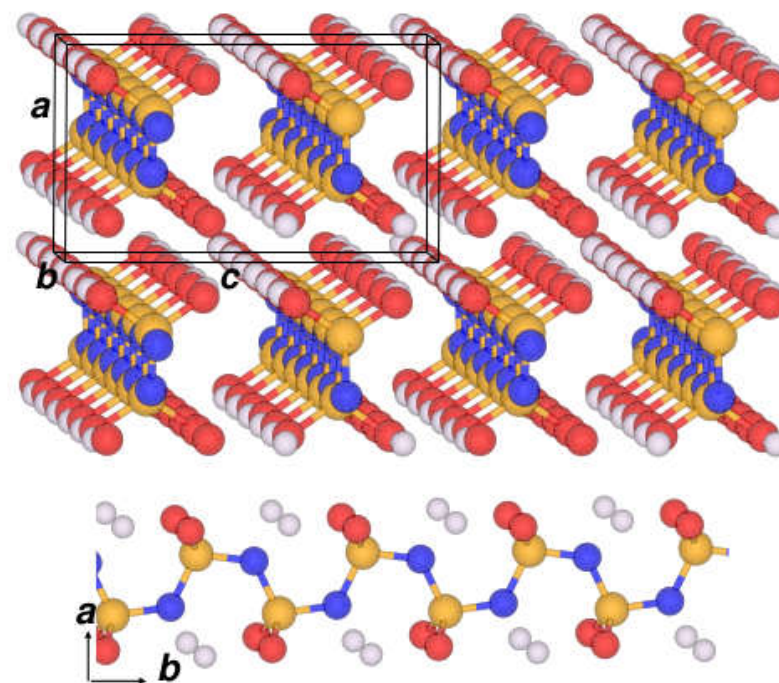
Fig. 7. Ball and stick diagrams for $LiPO_3$ in the $P2/c$ structure (20 formula units per unit cell) and $s1$-Li_2PO_2N in the $Pbcm$ structure (4 formula units per unit cell) from the calculated results. For each crystal diagram, a view of a horizontal chain axis is also provided for a single phosphate or phospho-nitride chain.

Computationally predicted structure

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Key

s_1-Li_2PO_2N *Pbcm*

○ Li

● N

● O

● P

● S
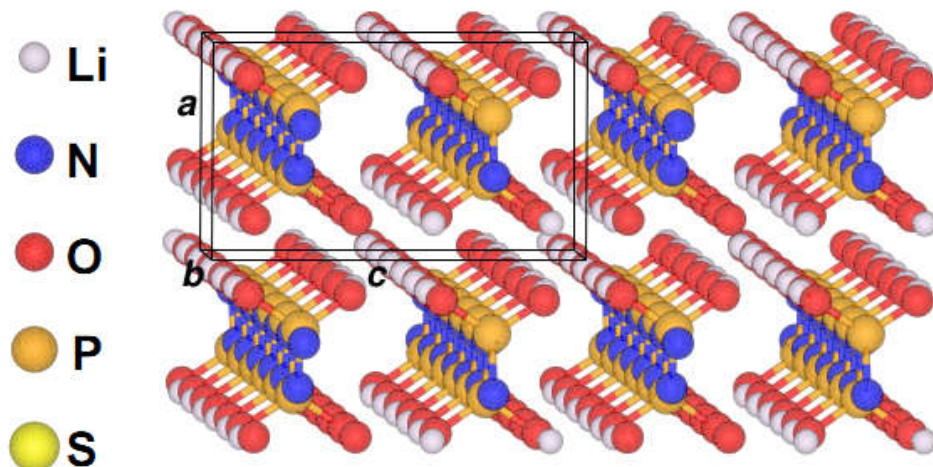
Calculations have now verified that the *SD* structure is more stable than the s_1 structure by 0.1 eV/FU.

Experimentally realized structure

SD-Li_2PO_2N *Cmc2$_1$*
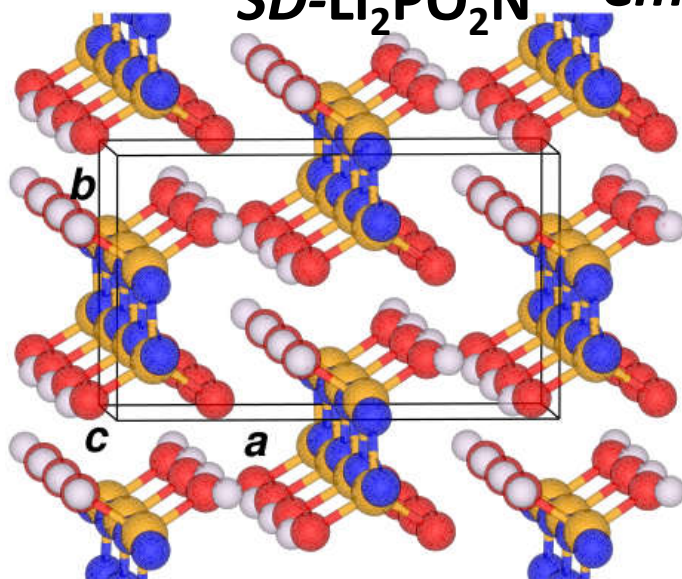
Synthesis of Li_2PO_2N by Keerthi Senevirathne, Cynthia Day, Michael Gross, and Abdessadek Lachgar (*SSI* **233**, 95-101 (2013)) High temperature solid state synthesis using reaction:

$$Li_2O + \tfrac{1}{5}P_2O_5 + \tfrac{1}{5}P_3N_5 \rightarrow Li_2PO_2N$$
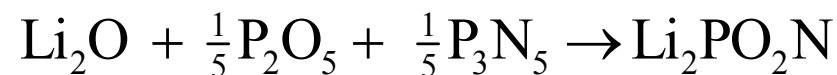
Systematic study of Li_xPS_y materials – (N. D. Lepley and N. A. W. Holzwarth, J. Electrochem. Soc. 159, A538 (2012), Phys. Rev. B 88, 104103 (2013))
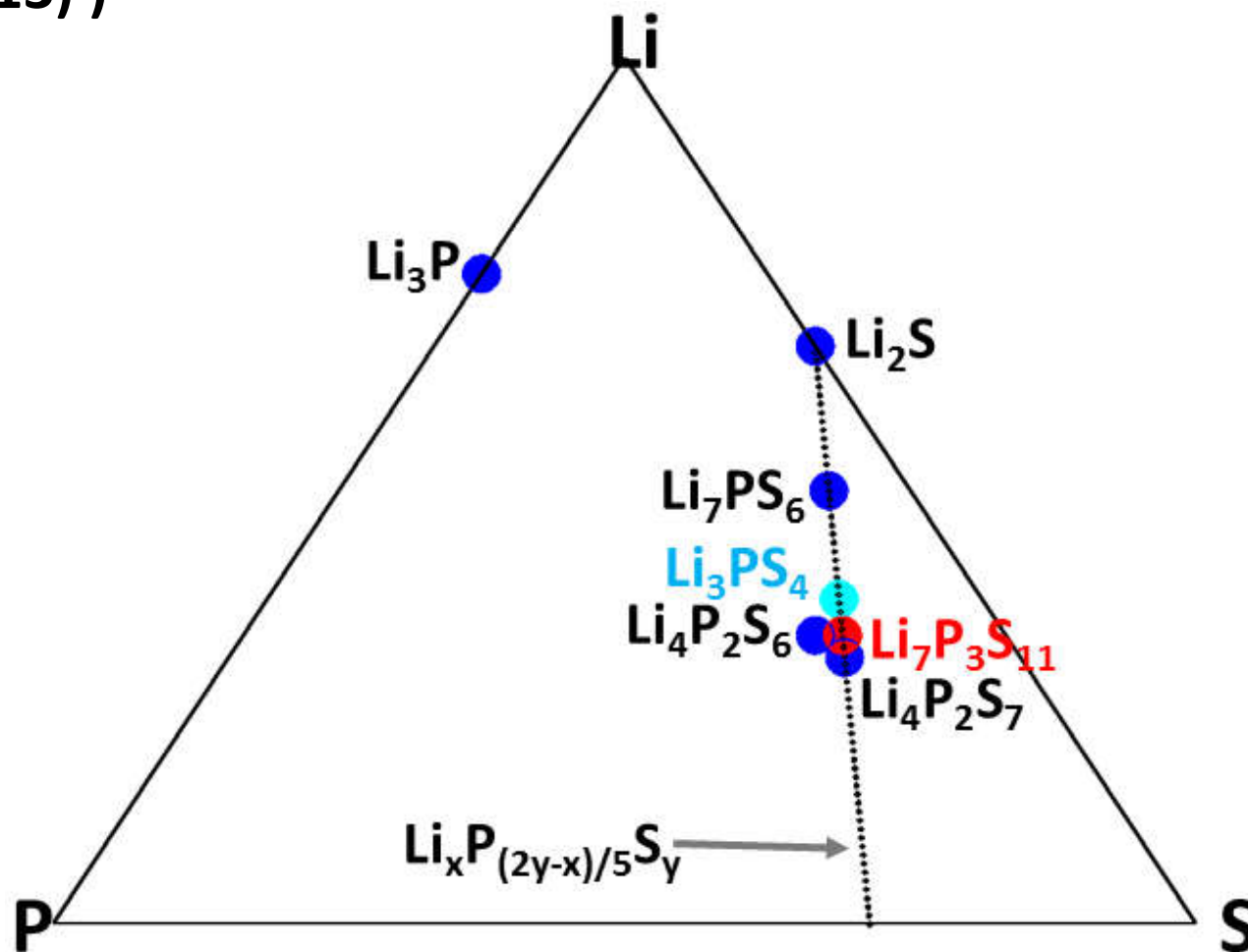
Some lithium thiophosphate crystal structures

$Li_4P_2S_7$

Key

○ Li
● N
● O
● P
○ S
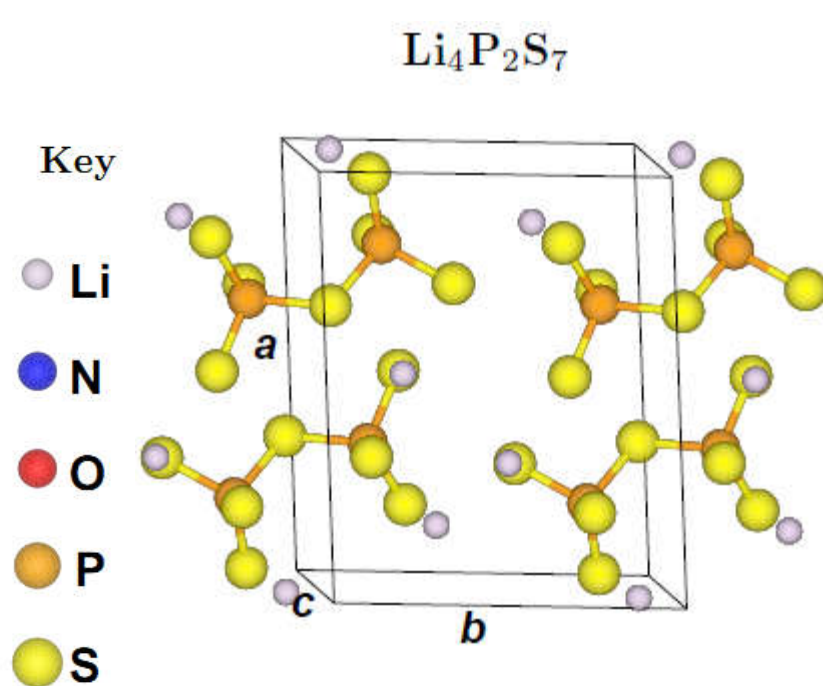
Experimentally amorphous; computationally metastable in $P\bar{1}$ structure

$Li_7P_3S_{11}$
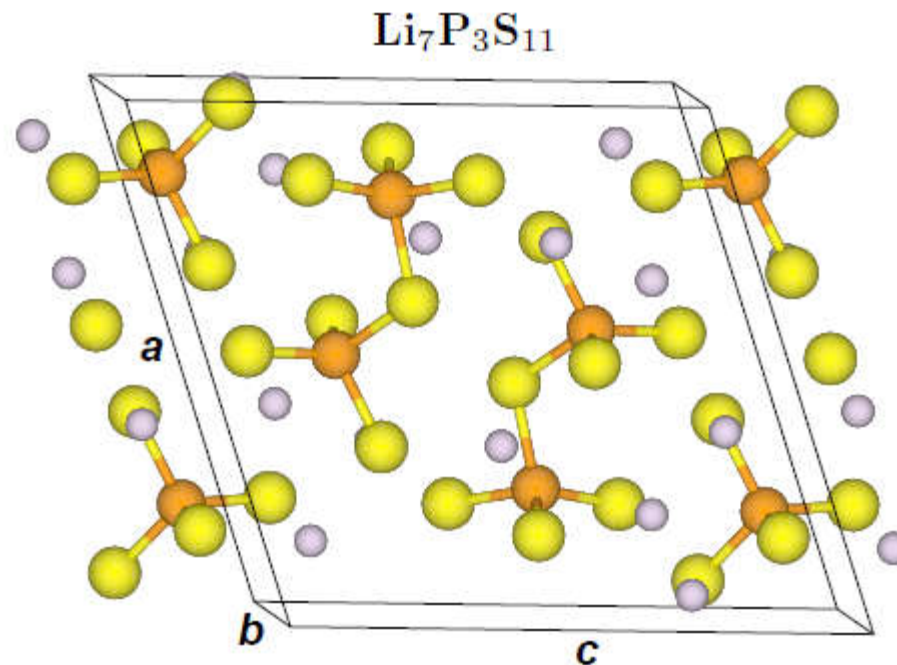
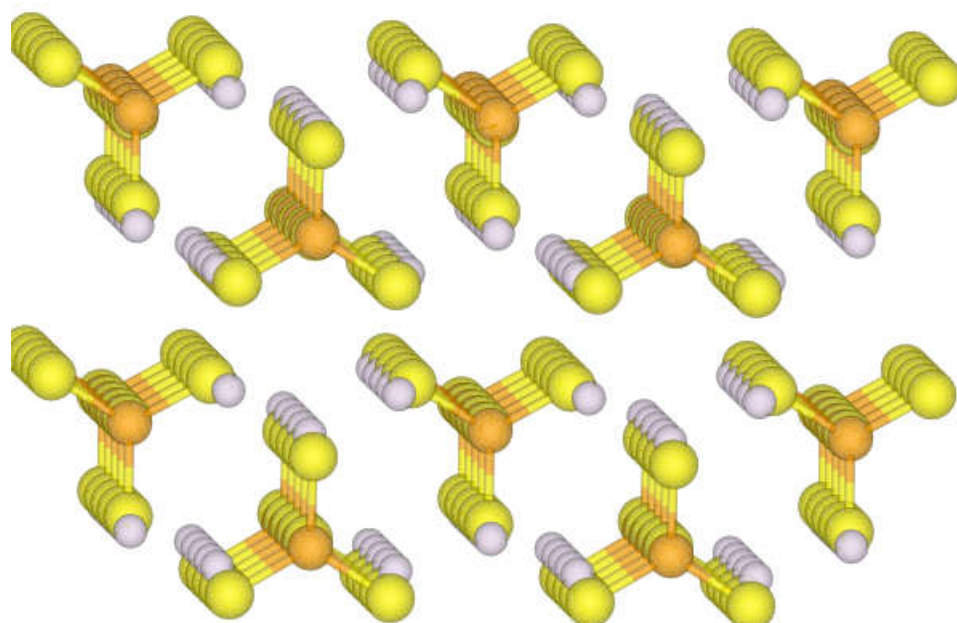Experimentally and computationally metastable in $P\bar{1}$ structure

Crystal structure of bulk Li$_3$PS$_4$ – γ-form Pmn2$_1$ (#31)

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Note: Li$_3$PS$_4$ is also found in the β-form with Pnma (#62) structure

- Li
- N
- O
- P
- S
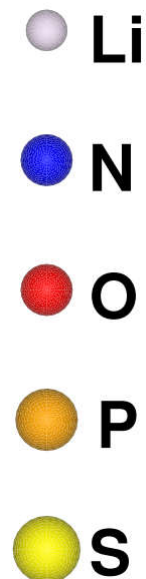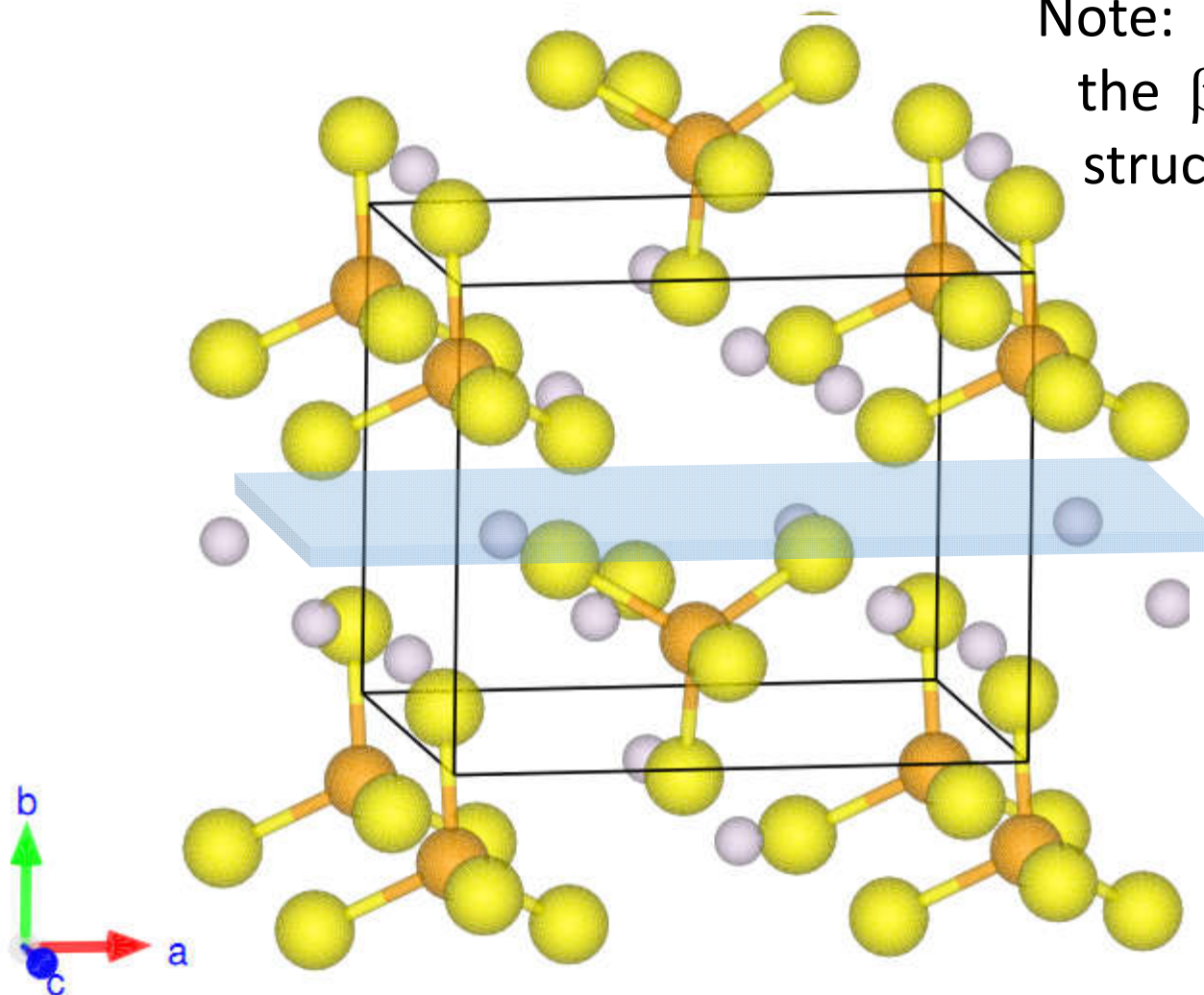
Simulations of ideal γ-Li$_3$PS$_4$ [0 1 0] surface in the presence of Li

Initial configuration:

Computed optimized structure:
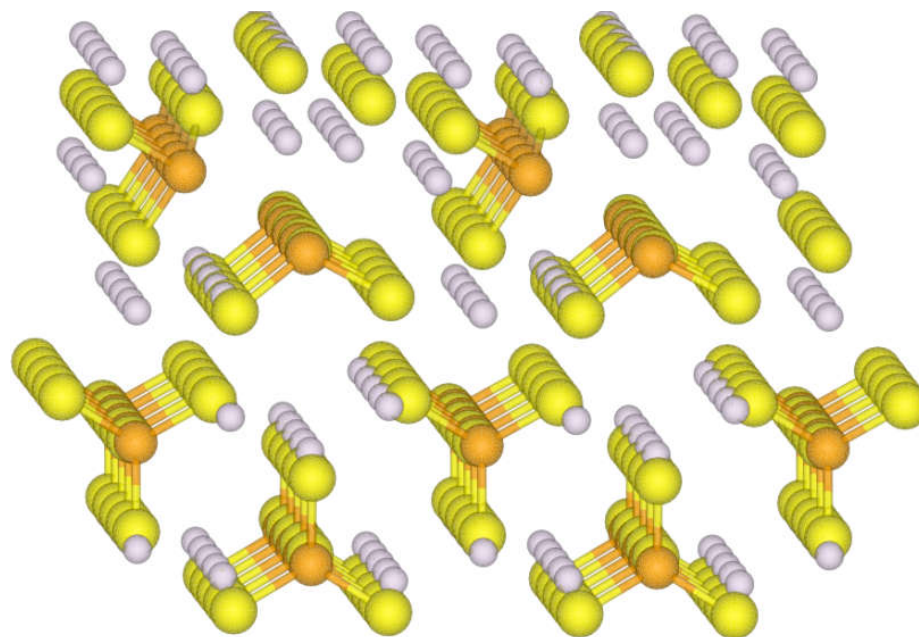
Energy diagram for ideal electrolyte/metal interface

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System Fermi level should fall within electrolyte band gap.

filled metal bands

empty metal bands

electrolyte valence

electrolyte conduction

Metal

Interface

Electrolyte

E_g

Energy
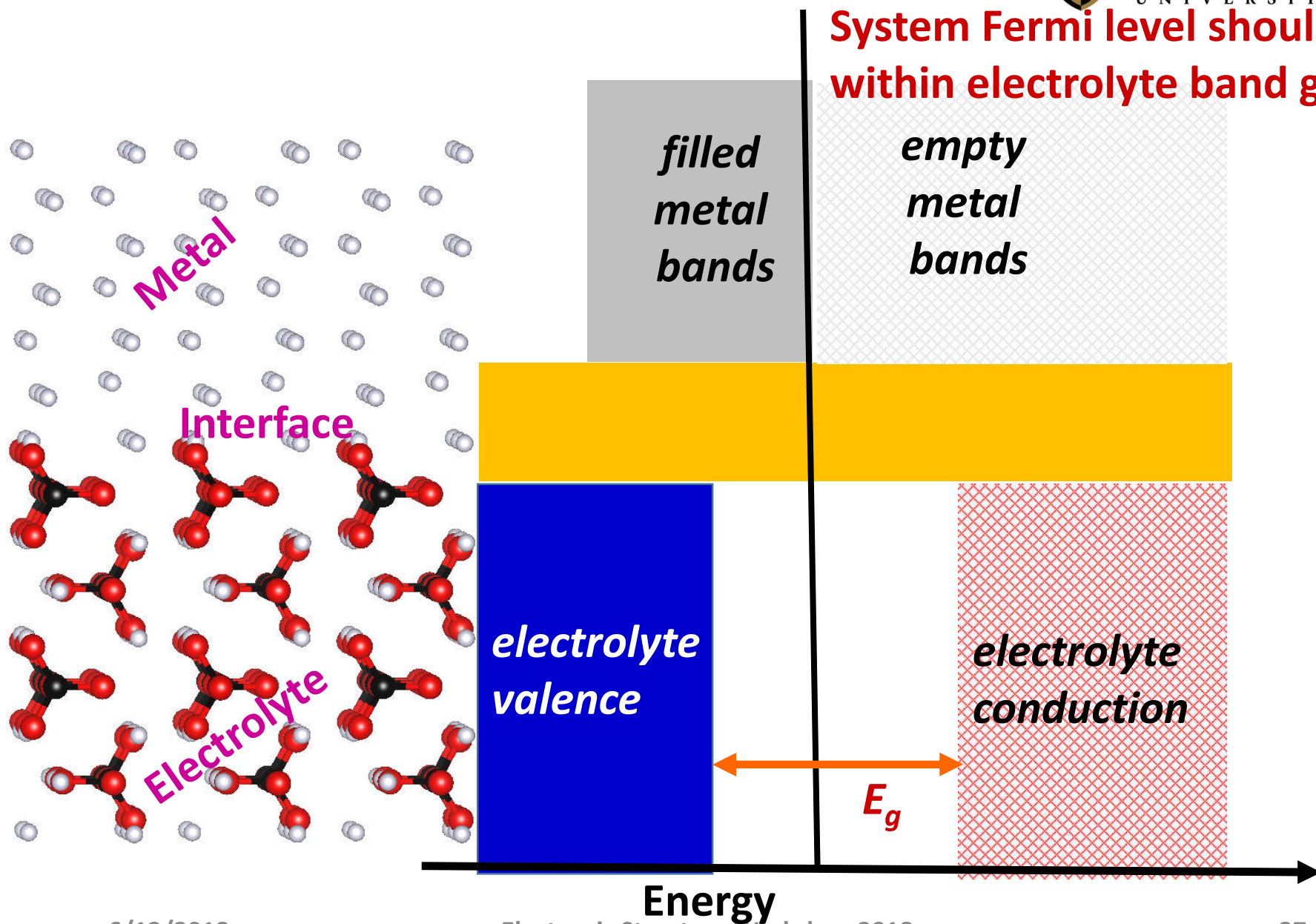
Possible interface configurations
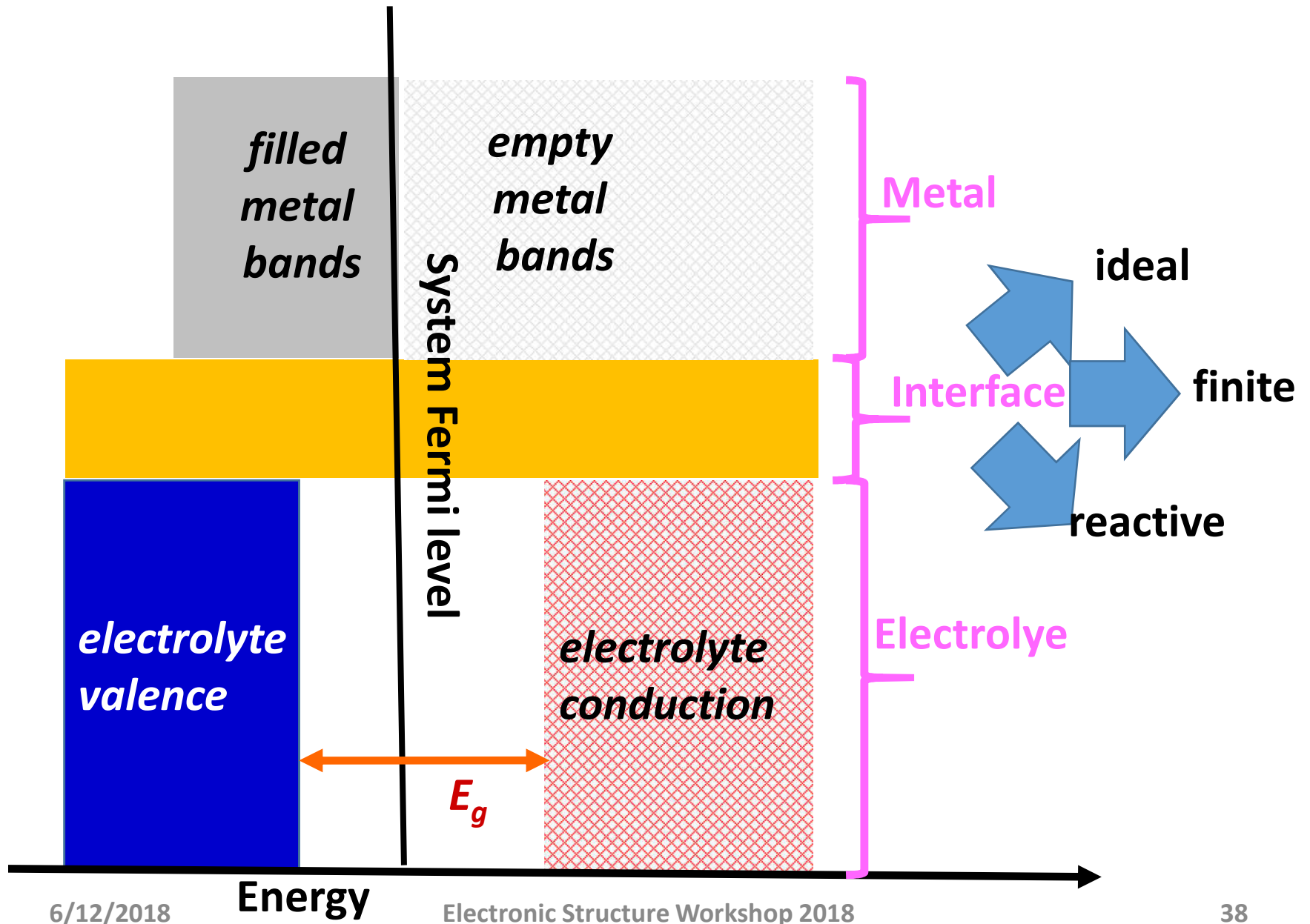
γ-Li₃PO₄/Li system
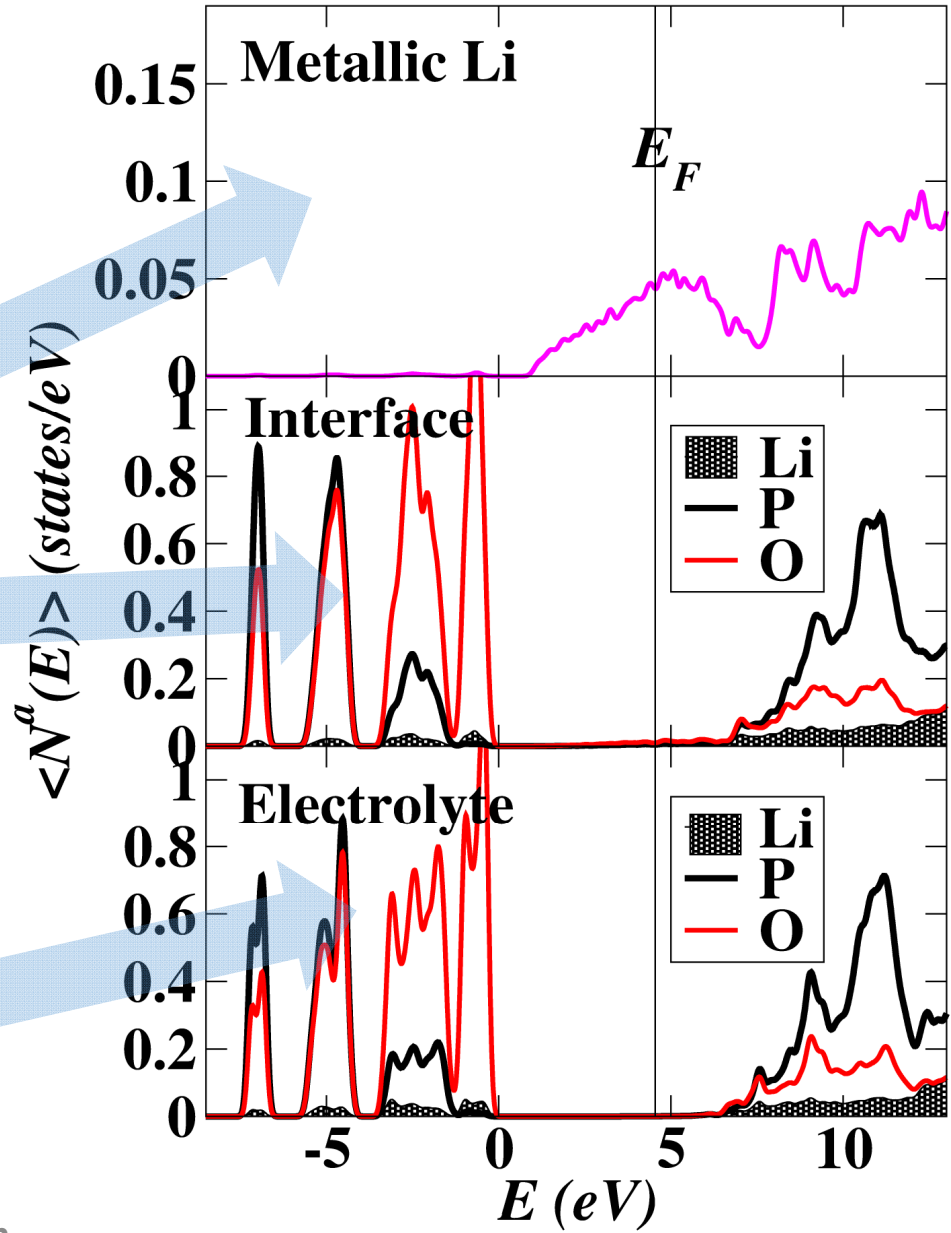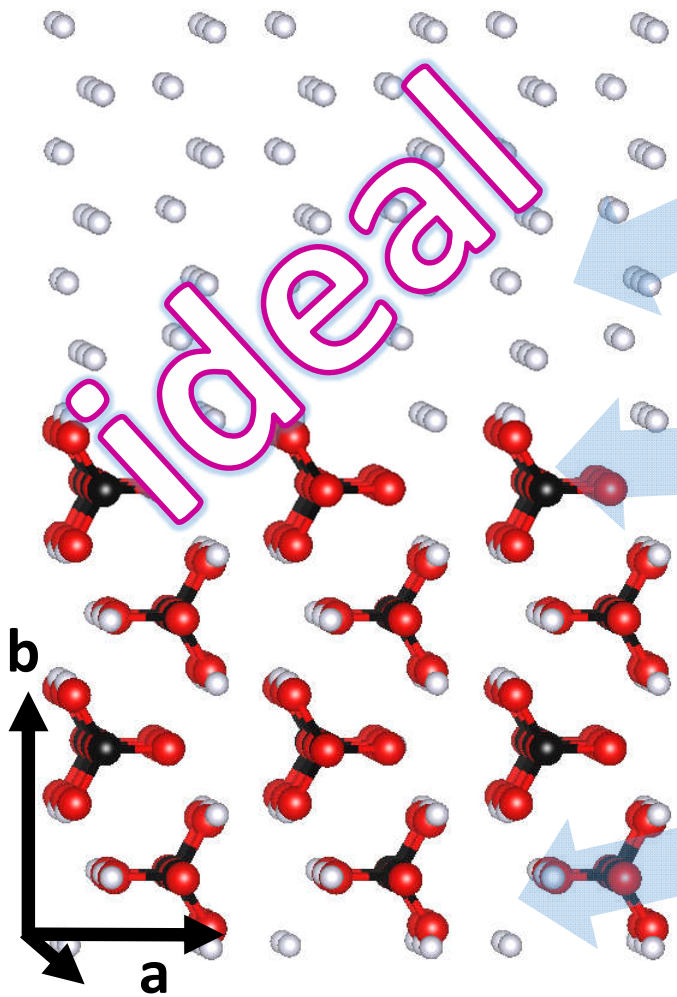
γ-Li₃PS₄/Li system

γ-Li$_3$PS$_4$/Li system

(Lepley (*et al.*) PRB 92 21401 (2015))
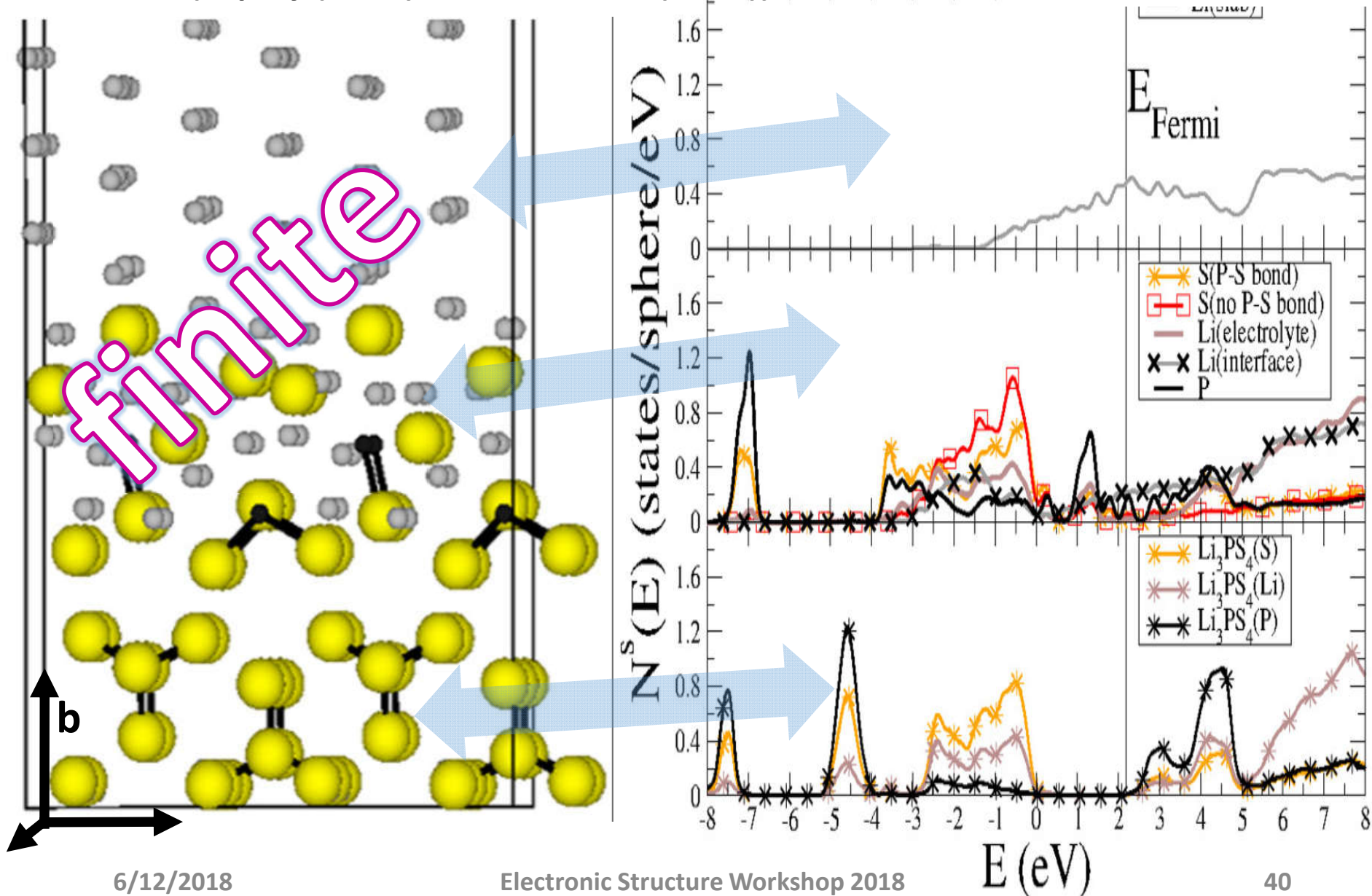
Summary of interface results

ideal   finite   reactive
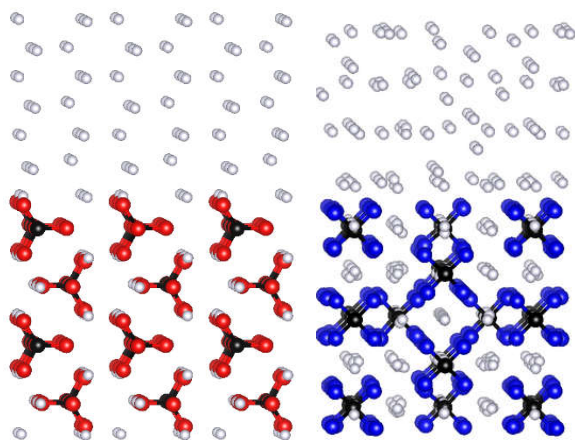
γ-Li_3PO_4 /Li Li_7PN_4/Li γ-Li_3PS_4/Li Na_3SbS_4/Na
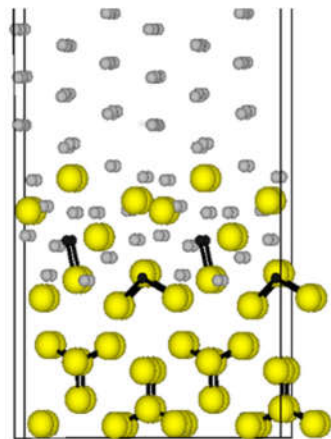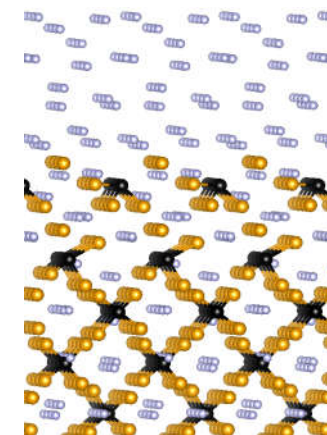
Thoughts on the role of simulations in developing battery technology

> ➢ Ideal research effort in materials includes close collaboration of both simulations and experimental measurements.

> ➢ For battery technology, there remain many opportunities for new materials development.