A formalism for modeling solid electrolyte/electrode interfaces using first principles methods*

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Ref: N. D. Lepley and N. A. W. Holzwarth, ***PRB* 92**, 214201 (2015)
N. D. Lepley, *Ph. D Thesis*, Wake Forest University, 2015.

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FOCUS: Solid state batteries – understanding interfaces between electrolytes and electrodes

- Develop and analyze a quantitative measure of interface energy, adjusting for the effects of lattice strain – $\tilde{\gamma}_{ab}^{\text{int}}$ which is particularly helpful for studying (meta-)stable interfaces

- Analyze the relationship of bulk and interface stability of Li_3PO_4/Li and Li_3PS_4/Li interfaces

- Analyze the effects of charge transfer across an interface

FOCUS: Solid state batteries – understanding interfaces between electrolytes and electrodes

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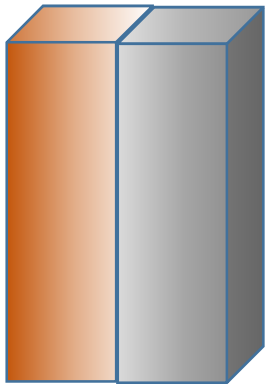
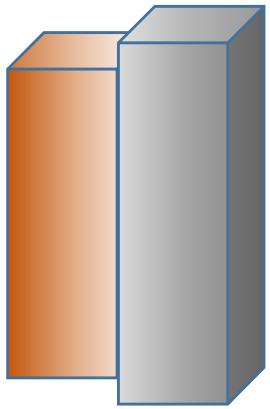
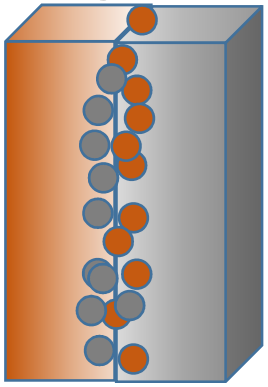
Ideal interface



Strained interface



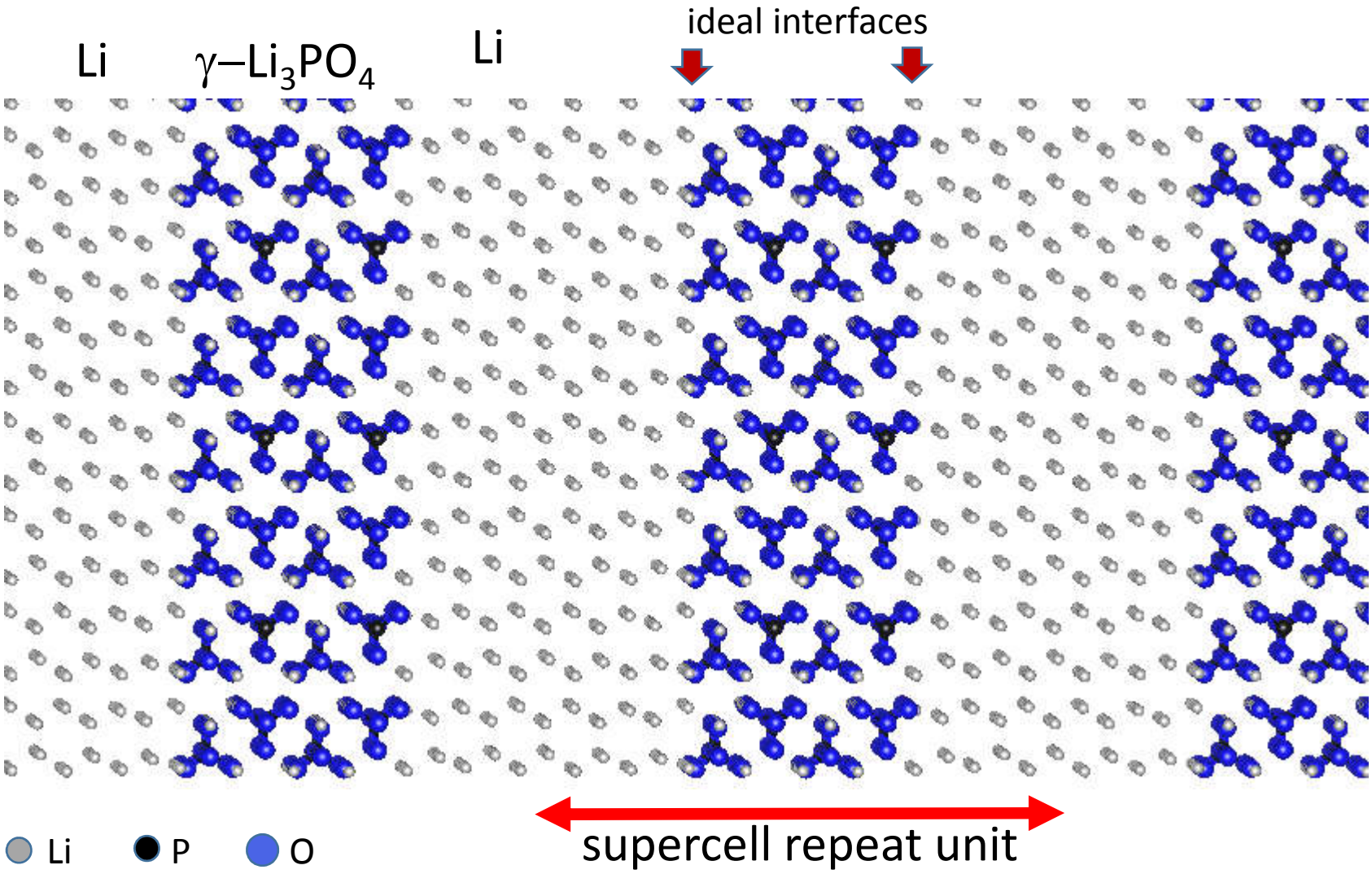
Interacting interface



Calculational methods:

- Density functional theory with LDA (Perdew, PRB 45, 13244 (1992))
- Projector Augmented Wave method (Blöchl, PRB **50**, 17953 (1994))
- ATOMPAW atomic datasets (Holzwarth, CPC **135**, 329 (2001))
- Quantum Espresso code (Giannozzi, J. Phy.:CM **21**, 395502 (2009))
- Plane wave cut off: $\left|\mathbf{k}+\mathbf{G}\right|^2 \leq 64\ \mathrm{bohr}^{-2}$
- Nudged elastic band simulations (Henkelman, JCP **113**, 9978 (2000)
- Visualization software: Kokalj, Comp. Mater. Sci. **28**, 155 (2003) and Momma, Acta Cryst. **44**, 1272 (2011)

It is convenient to model the interface between a solid electrolyte and solid electrode in the slab geometry using a periodic simulation cell:

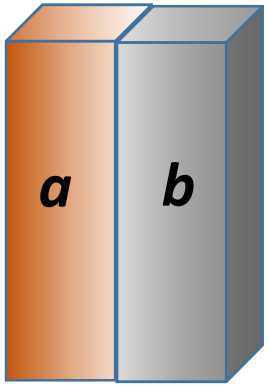


Within any given periodic simulation cell with n_a units of material a and with n_b units of material b, we can define an interface energy:

$$\tilde{\gamma}_{ab}\left(\tilde{\Omega}, n_a, n_b\right) = \frac{\tilde{E}_{ab}\left(\tilde{\Omega}, A, n_a, n_b\right) - n_a E_a - n_b E_b}{A}$$

area of interface within supercell

bulk energies

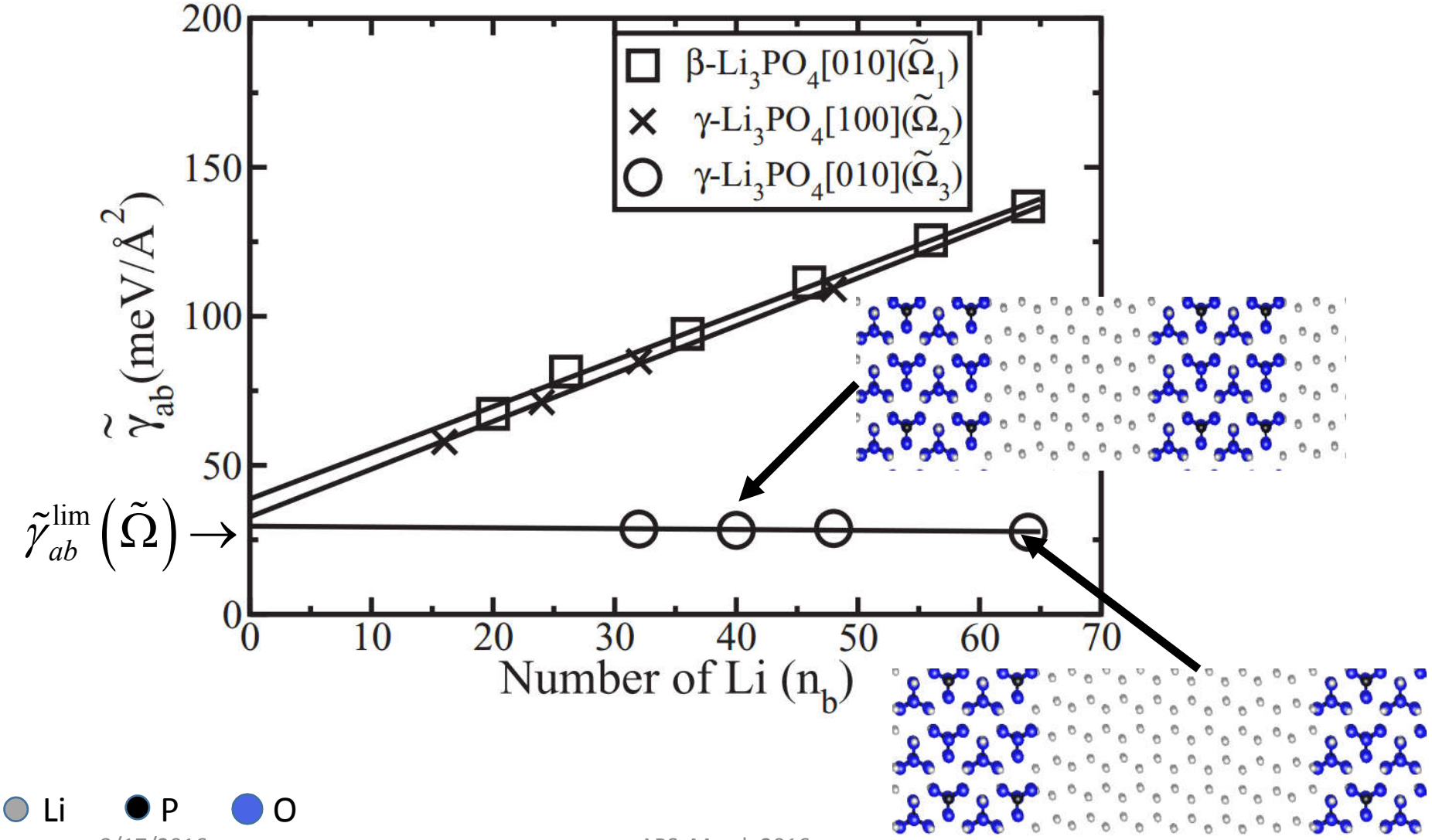


In order approximately remove the effects of lattice strain:

- Design the supercell to be commenserate with lattice a
- Now the strain will scale with the amount of material b

$$\Rightarrow \tilde{\gamma}_{ab}\left(\tilde{\Omega}, n_a, n_b\right) = \tilde{\gamma}_{ab}^{\lim}\left(\tilde{\Omega}\right) + n_b \sigma$$

Lepley's linear equation for the interface energy: $\tilde{\gamma}_{ab}\left(\tilde{\Omega}, n_a, n_b\right) = \tilde{\gamma}_{ab}^{\lim}\left(\tilde{\Omega}\right) + n_b\sigma$



System	$\tilde{\gamma}_{ab}^{\lim}$ (meV/Å²)	σ (meV/Å²)
$Li_2O[110]/Li(\Omega_1)$	30	6.1
$Li_2O[110]/Li(\Omega_2)$	26	0.2
$Li_2S[110]/Li(\Omega_3)$	19	0.2
$Li_2S[100]/Li(\Omega_4)$	19	0.0
γ–Li_3PO_4 [010]/$Li(\Omega_3)$	31	0.0
γ–Li_3PS_4 [010]/Li_2S [110]	16	1.0
γ–Li_3PS_4 [010]/Li	-216	-0.1

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γ–Li_3PS_4 [010]/Li_2S [110]

Li P S

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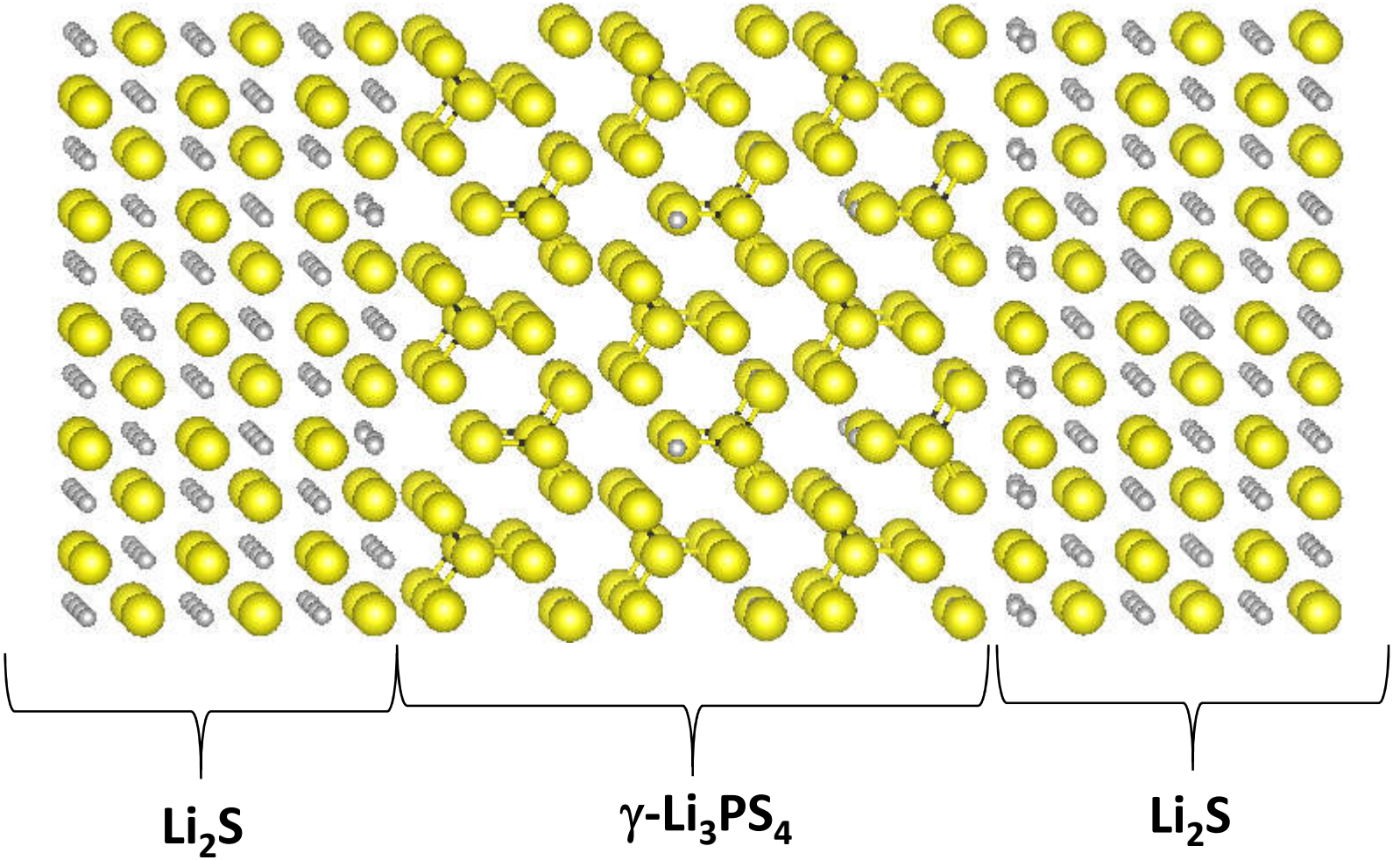

Stable interface; composite electrolyte system

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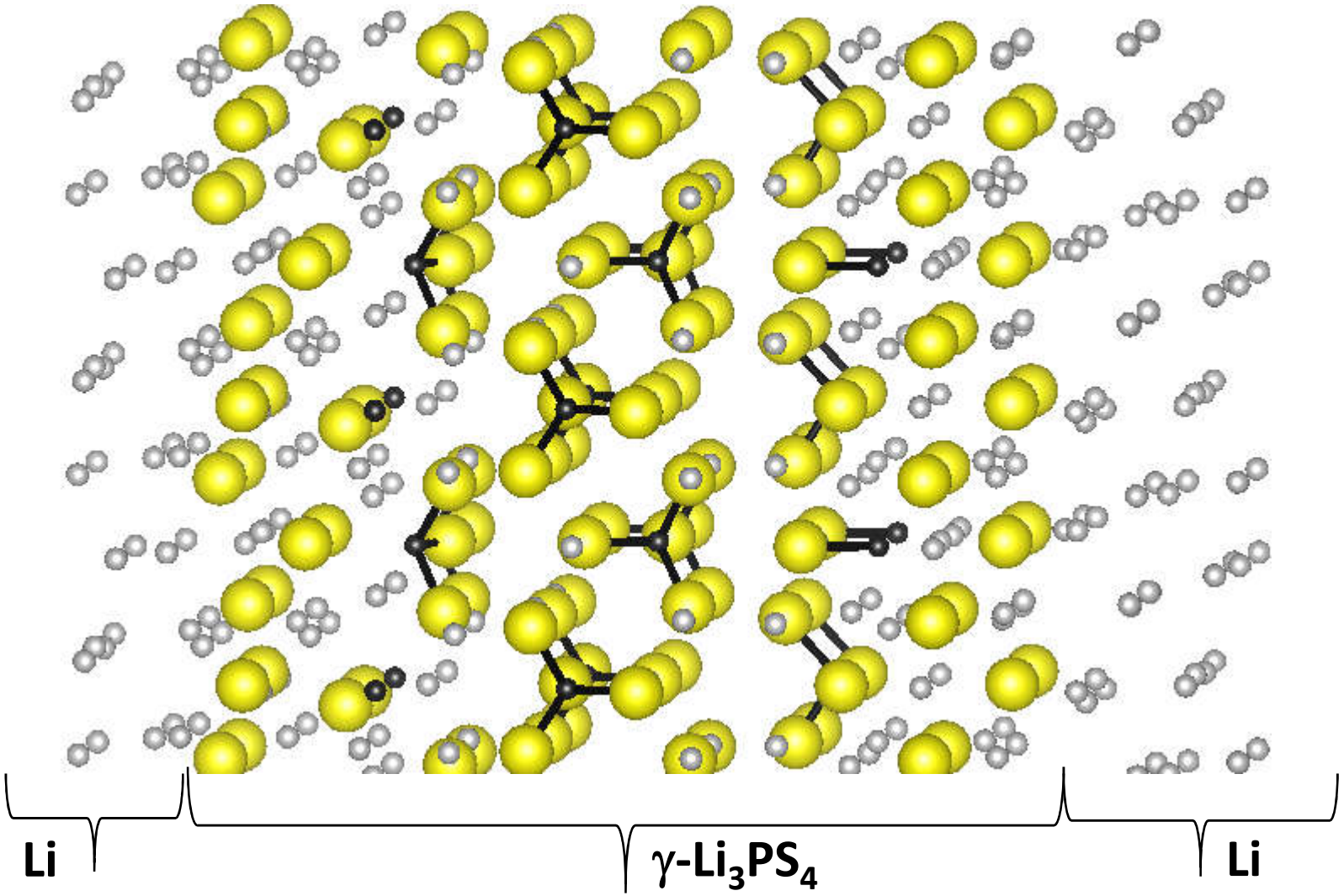
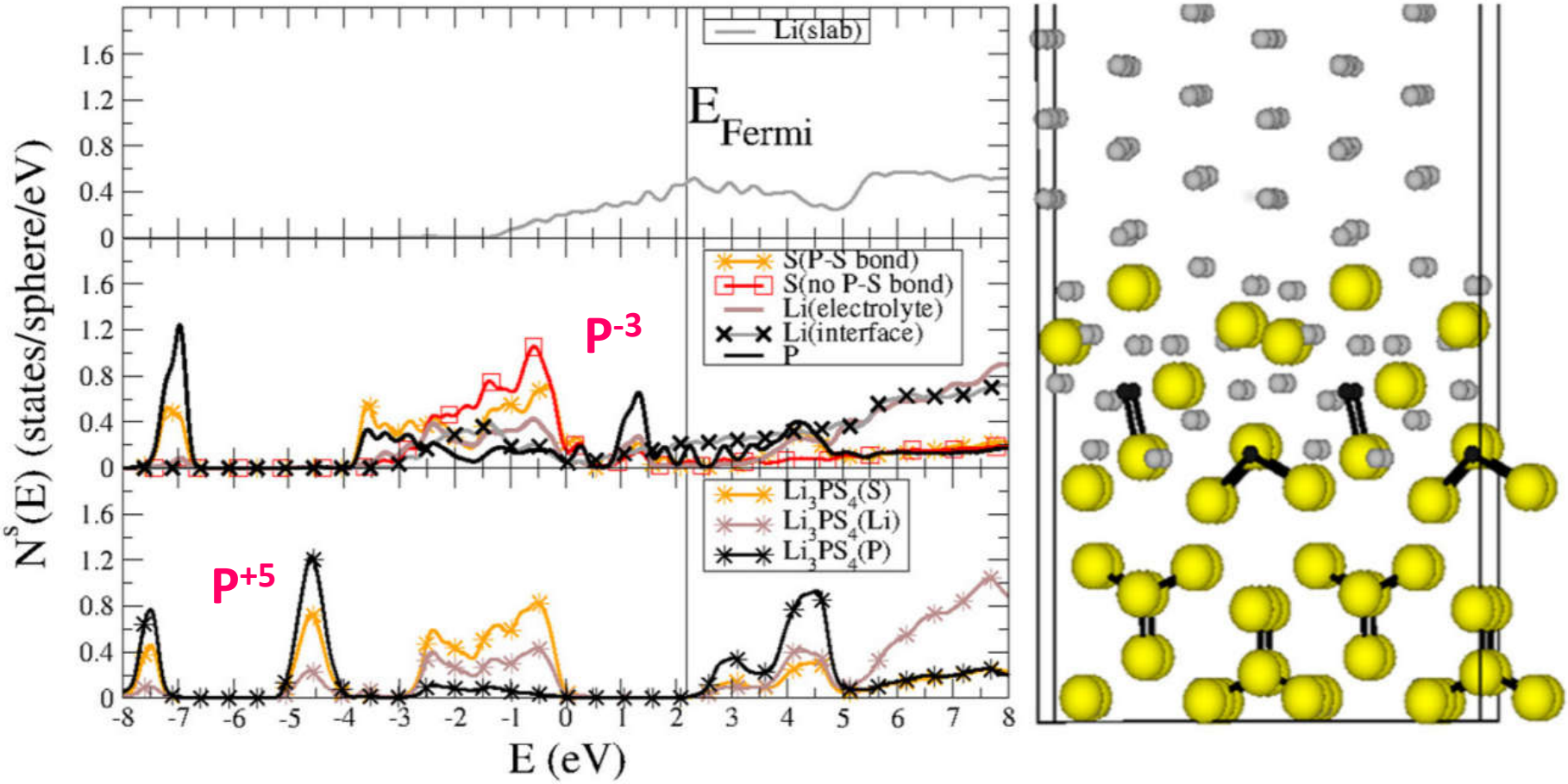
Li P S



Initially unstable interface; (meta)-stable buffer layer formed

Partial density of states analysis of unstable Li_3PS_4/Li interface:



$$Li_3PS_4 + 8Li \longrightarrow Li_3P + 4Li_2S + 12.30\ eV$$

Bulk reactions from estimated heats of formation

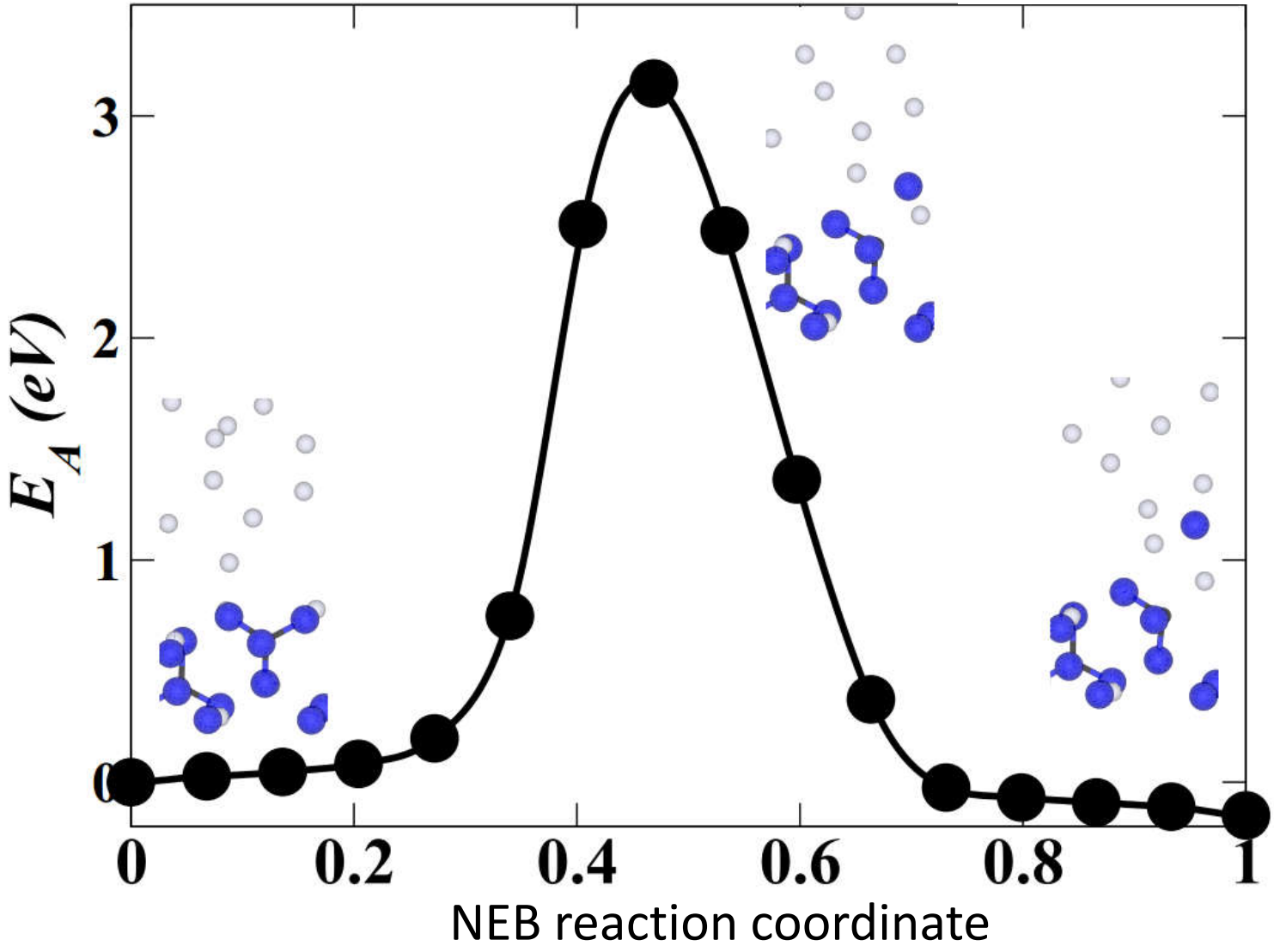
$$Li_3PS_4 + 8Li \longrightarrow Li_3P + 4Li_2S + 12.30\ eV$$

Decomposition at interface

$$Li_3PO_4 + 8Li \longrightarrow Li_3P + 4Li_2O + 6.64\ eV$$

(Meta-)stable interface

Evidence of kinetic barrier at Li_3PO_4/Li interface



Modeling of charge transfer in Li_3PO_4/Li system

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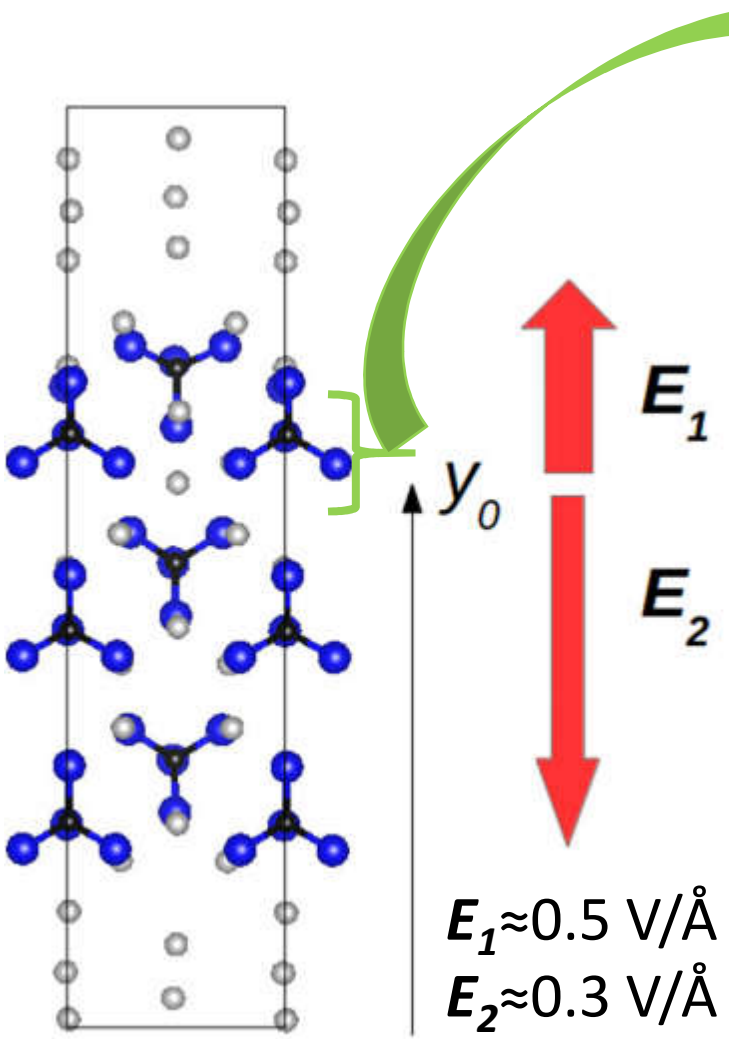

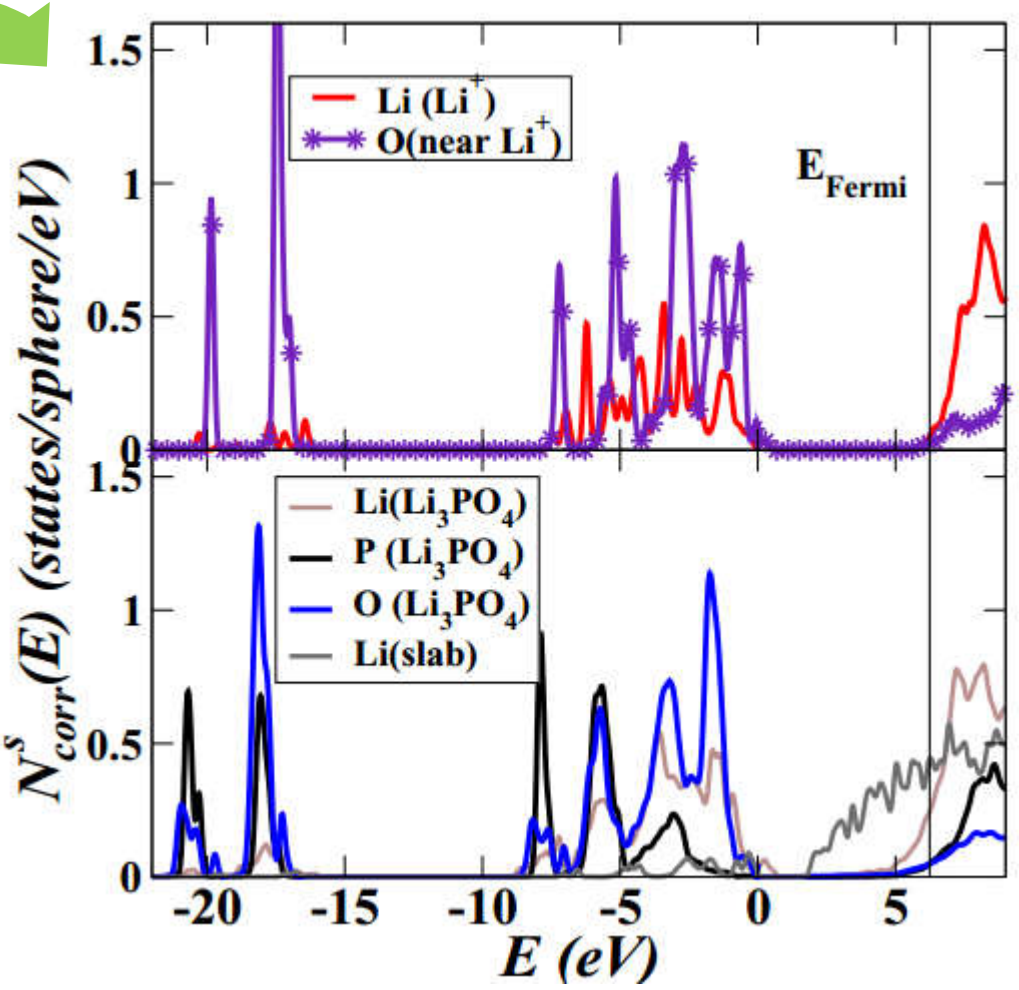

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Summary and conclusions

- A practical scheme was developed to compute an intensive measure of the interface interaction $\tilde{\gamma}_{ab}^{\text{int}}$, explicitly accounting for the effects of lattice stain.
- Discussed bulk reactivity as related to the interface stability of the interfaces of
  - Li_3PO_4/Li (having a significant kinetic barrier to decomposition)
  - Li_3PS_4/Li (having localized decomposition).
- Discussed effects of charge transfer across Li_3PO_4/Li interfaces – small supercells result in large internal electrostatic fields