Role of exchange-correlation functionals on migration barrier predictions in battery materials

Sai Gautam Gopalakrishnan[1], Reshma Devi[1], Baltej Singh[2], Pieremanuele Canepa[2,3]

[1]Department of Materials Engineering, Indian Institute of Science, Bengaluru 560012, India
[2]Department of Materials Science and Engineering, National University of Singapore, Singapore 117575
[3]Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117575

saigautamg@iisc.ac.in
https://sai-mat-group.github.io

INTRODUCTION

- Next generation of energy storage technologies require both high energy and power densities
- Critical factor that influences rate (power) performance in intercalation batteries is the diffusivity (D) of electroactive ions within solid host frameworks
  - $D = D_o \exp\left(-\frac{E_m}{RT}\right)$; E_m is the migration barrier governing ionic diffusion[1]
- Theoretical estimates of E_m: density functional theory (DFT) + nudged elastic band (NEB)[2]
  - How does choice of exchange-correlation (XC) functional in DFT affect E_m?
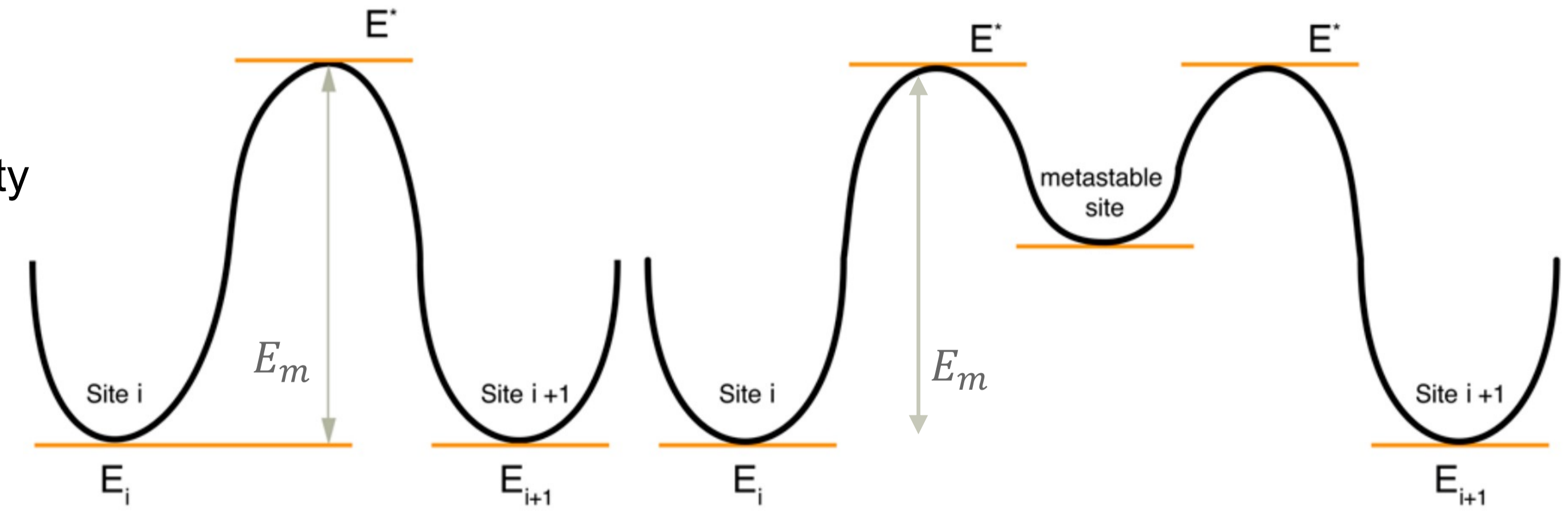
METHODS

- All calculations done with Vienna ab initio simulation package (VASP[3])
- NEB settings: 7 images, spring force of 5 eV/Å, force converged within |0.05| eV/Å, limited memory Broyden-Fletcher-Goldfarb-Shannon optimizer[4]
- 3 handles that influence E_m explored

XC Choice
- Generalized gradient approximation (GGA)
  - Perdew-Burke-Ernzerhof[5]
- Strongly constrained and appropriately normed (SCAN)[6]
- GGA+U and SCAN+U[7]
  - U value from previous works[8,9]
  - For electrodes only

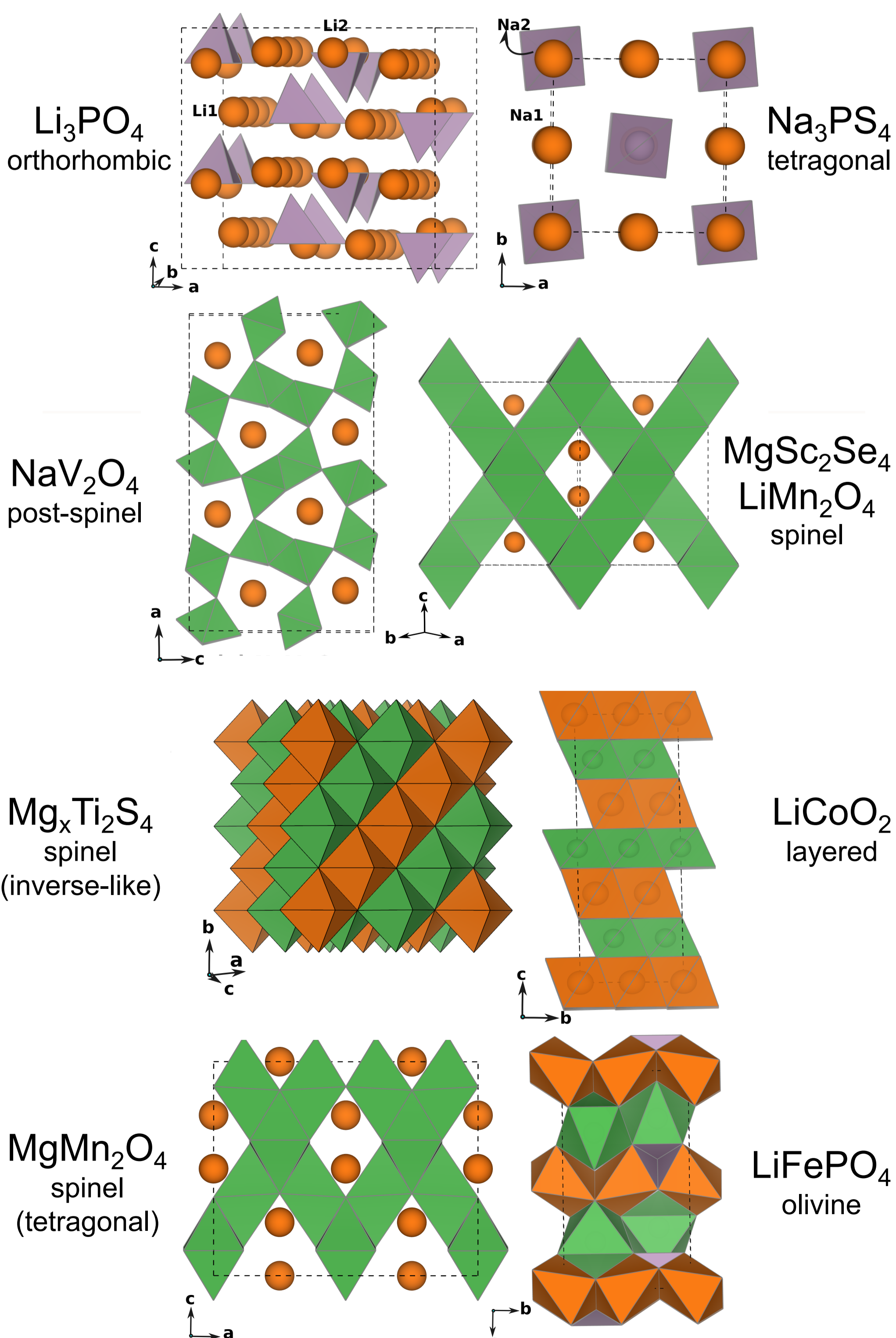**Addition of uniform background charge (NE or ne)**
- For solid electrolytes only

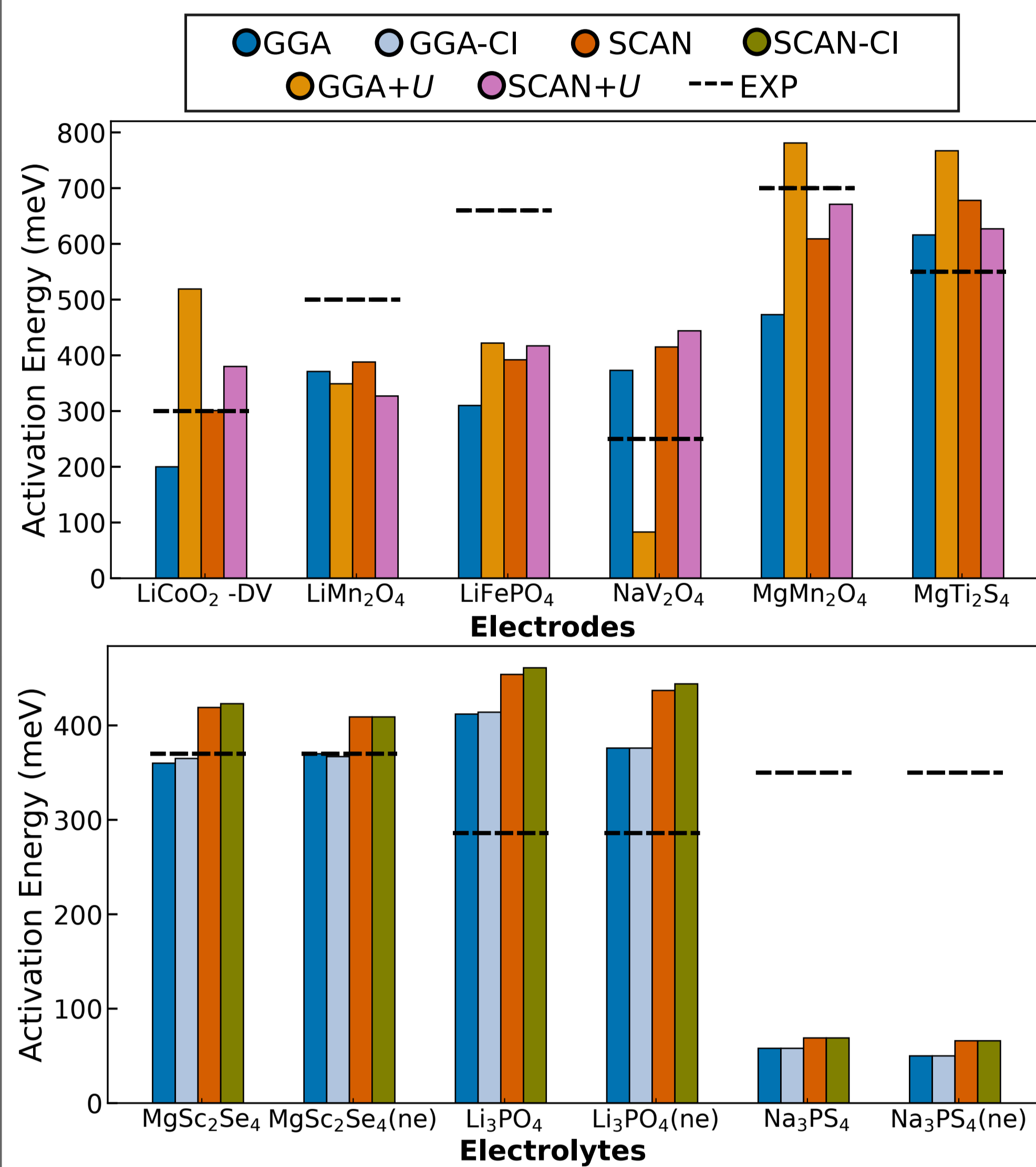**Addition of climbing image (CI) approximation**
- For solid electrolytes only

SYSTEMS

- 9 distinct systems: 6 electrodes and 3 solid electrolytes
- Choice of system motivated by
  - Experimental data availability
  - Heterogeneity of intercalation ion
  - Diversity of structural frameworks
- All initial structures from inorganic crystal structure database[10]


Li_3PO_4 orthorhombic

Na_3PS_4 tetragonal

NaV_2O_4 post-spinel

$MgSc_2Se_4$
$LiMn_2O_4$ spinel

$Mg_xTi_2S_4$ spinel (inverse-like)

$LiCoO_2$ layered

$MgMn_2O_4$ spinel (tetragonal)

$LiFePO_4$ olivine

RESULTS

Legend: GGA, GGA-CI, SCAN, SCAN-CI, GGA+U, SCAN+U, EXP

Top: Activation Energy (meV) vs Electrodes: LiCoO₂ -DV, LiMn₂O₄, LiFePO₄, NaV₂O₄, MgMn₂O₄, MgTi₂S₄

Bottom: Activation Energy (meV) vs Electrolytes: MgSc₂Se₄, MgSc₂Se₄(ne), Li₃PO₄, Li₃PO₄(ne), Na₃PS₄, Na₃PS₄(ne)

KEY TRENDS

- SCAN has lower mean absolute error (MAE, ~140 meV) compared to other functionals (> 145 meV)
- Addition of NE/ne or CI does not affect E_m in solid electrolytes
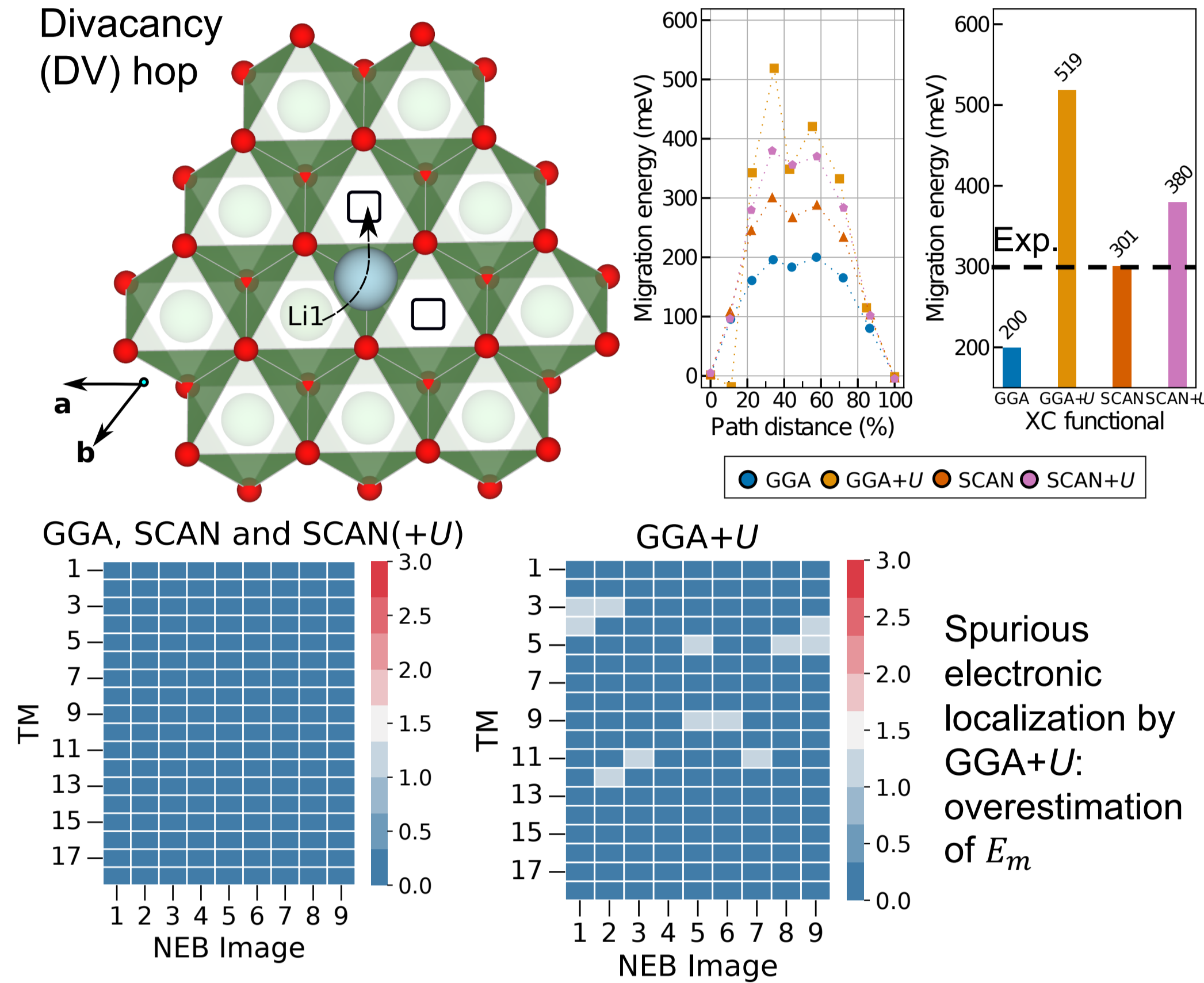- SCAN E_m > GGA E_m
- SCAN+U E_m < GGA+U E_m (except NaV₂O4)

EXAMPLE 1: $MgMn_2O_4$
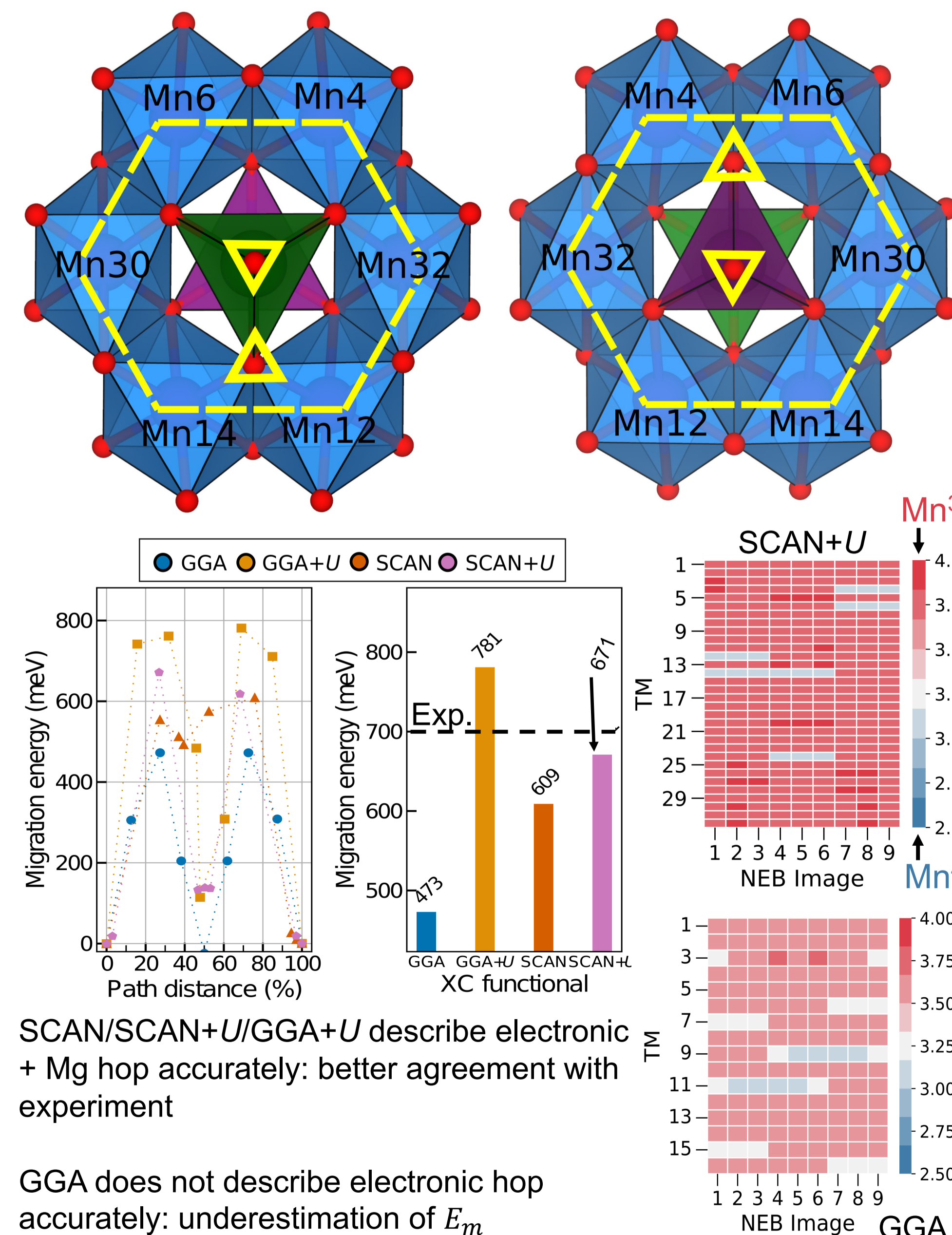
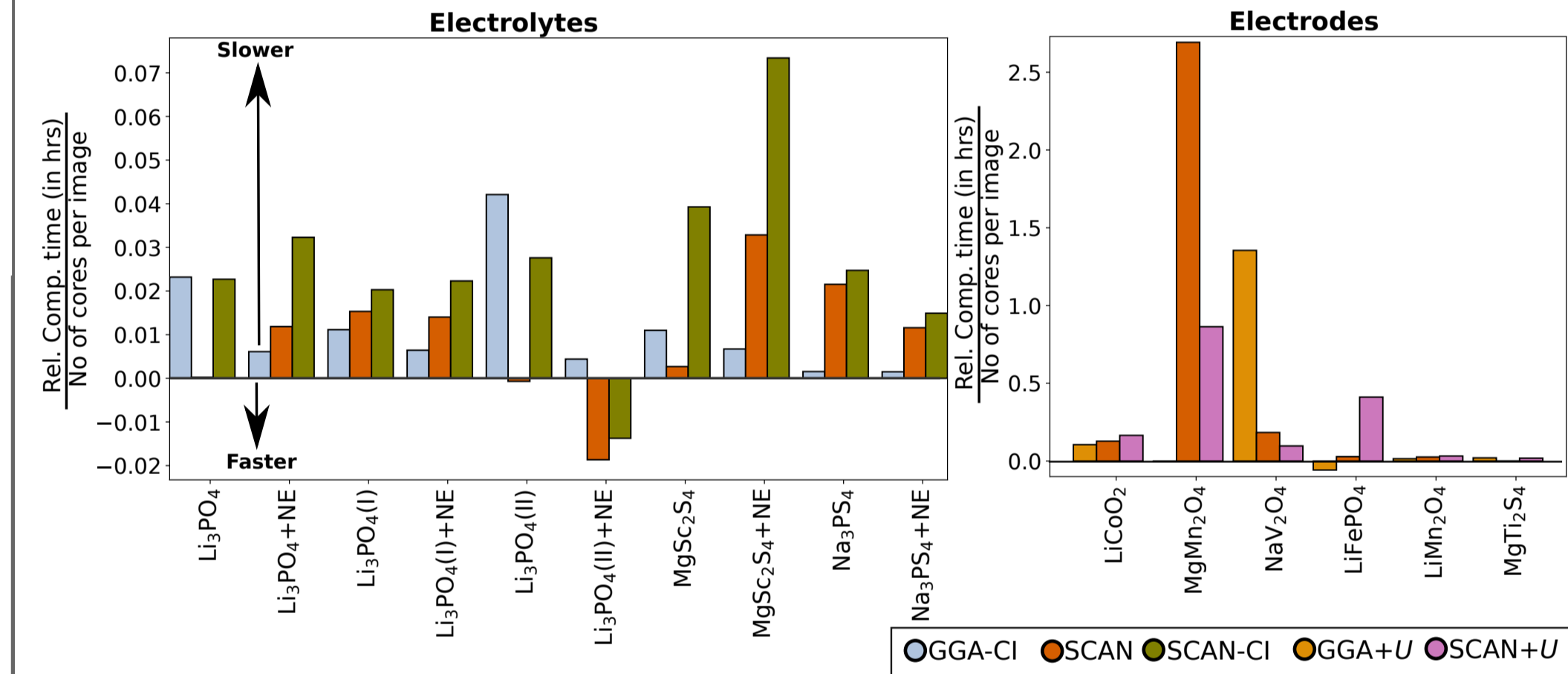SCAN/SCAN+U/GGA+U describe electronic + Mg hop accurately: better agreement with experiment

GGA does not describe electronic hop accurately: underestimation of E_m

EXAMPLE 2: $LiCoO_2$

Divacancy (DV) hop

Spurious electronic localization by GGA+U: overestimation of E_m

COMPUTATIONAL PERFORMANCE

- Computational time with GGA/GGA+U ~75% faster than SCAN
- SCAN faster than SCAN+U
- Significant convergence difficulties with SCAN and SCAN+U

CONCLUSION

Migration barriers are key in determining rate performance of batteries: need accurate computations to predict

We explored accuracy and computational performance of various XC frameworks in 6 electrodes and 3 solid electrolytes

- SCAN has better numerical accuracy than other functionals on average: but notable exceptions exist + convergence difficulties
- Addition of NE/ne or CI does not influence E_m

GGA for "*quicker*" estimate   SCAN for "*better*" accuracy

ACKNOWLEDGEMENTS

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