

BOND-VALENCE ENERGY LANDSCAPES A SIMPLE COMPUTING TOOL FOR ASSESSING IONIC CONDUCTIVITY IN BATTERY MATERIALS

The Program Bond_Str

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An investigation of the structural properties of Li and Na fast ion conductors using high-throughput bond-valence calculations and machine learning

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The Bond-Valence Sum method

The bond-valence method is a development of the Pauling rules. The bond-valence of a bond A-X can be written as:

$$s_{A-X} = \exp\left(\frac{R_0 - R_{A-X}}{b}\right)$$

Where R_0 and b ($\approx 0.37\text{\AA}$) are tabulated parameters characteristic of the pair A-X and R_{A-X} is the bond length.

The total valence V_A of the cation A (ideally equal to the magnitude of the formal charge) coordinated by N_C anions X is given by the bond-valence sum (BVS):

$$V_A = \sum_{i=1}^{N_C} s_{A-X_i} \approx V_A^{ideal} \text{ (formal charge)}$$

<http://www.iucr.org/resources/data/data-sets/bond-valence-parameters>

I. D. Brown, *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*, Oxford University Press, 2002.

The Bond-Valence Sum method

- The bond valence approach is frequently used to validate newly determined crystal structures by the calculation of the Global Instability Index (GII)

$$GII^2 = \frac{1}{N_{cell}} \sum_{i=1}^{N_{asym}} m_i (BVS_i - V_i^{ideal})^2$$

where N_{cell} is the total number of atoms in the unit cell, N_{asym} is the number of atoms in the asymmetric unit, and m_i is the multiplicity of the site i .

- Charge ordering is often quantified using bond-valence
- These calculations are implemented in a variety of computing programs: FullProf, LHPM-Rietica, ICSD web-based search, etc.

Ionic conduction and the BVS method

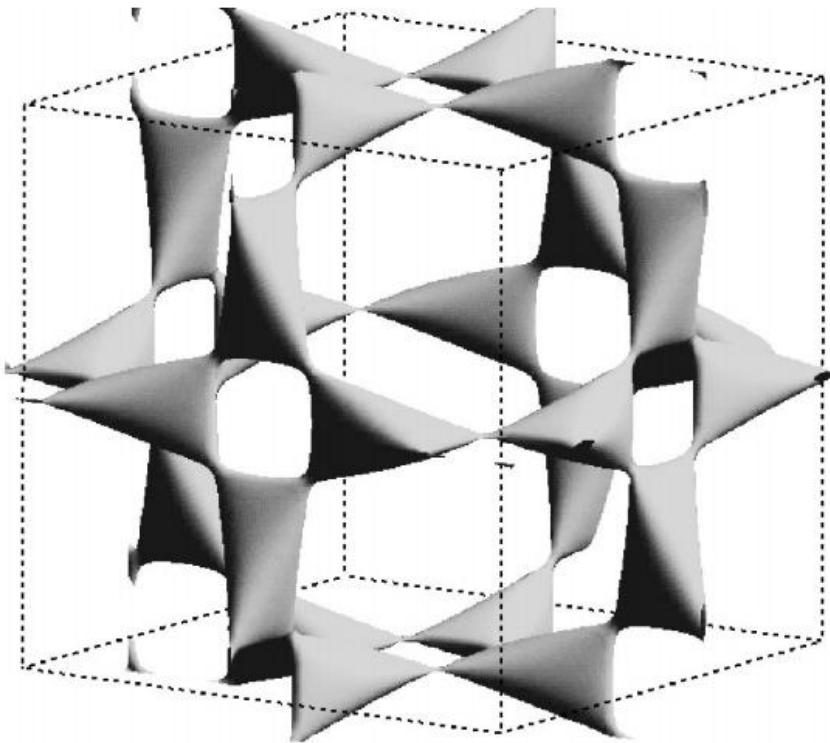
The bond-valence method can be used for assessing the ionic conduction path from the knowledge of the crystal structure.

Low-energy transport pathways for the motion of ions between equilibrium sites **should correspond to a sequence of positions for which the BVS mismatch: $\Delta V(r) = |\text{BVS}(r) - V^{\text{ideal}}(r)|$ remain as small as possible**, so a simple geometric calculation allows to figure out possible ionic conduction paths.

Examples of the BVS isosurfaces

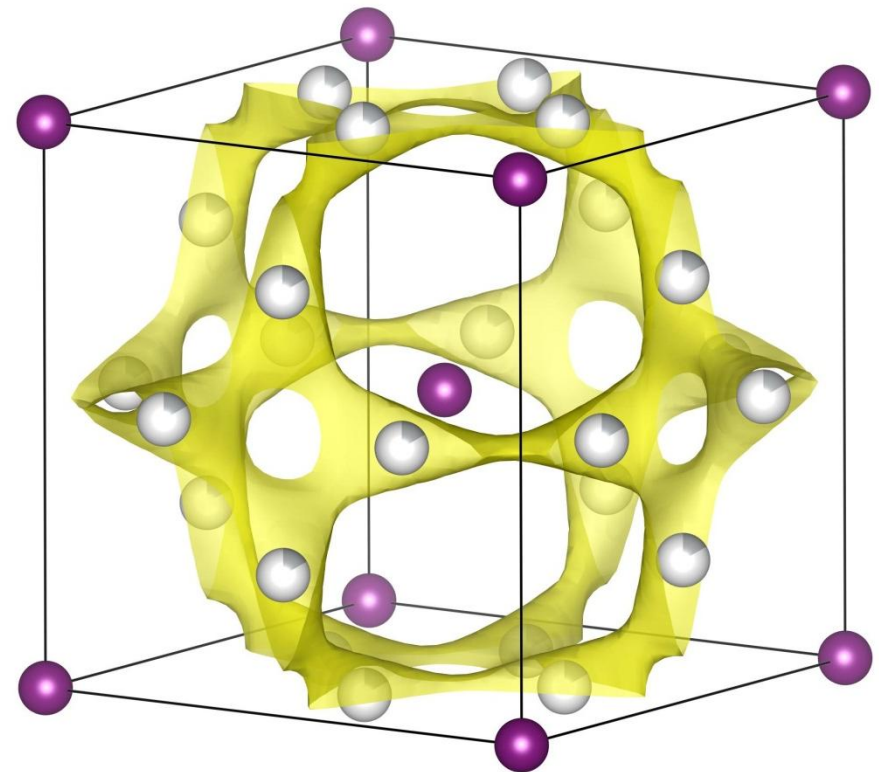
Differential bond-valence mismatch in Ag-I

$$v_{Ag-I} = \exp\left(\frac{2.08\text{\AA} - R_{Ag-I}}{0.53\text{\AA}}\right), R_{cut} = 8\text{\AA}$$



Bond valence isosurface

for α-AgI ($\Delta V=0.05$ val. un.)



Bond valence isosurface

for α-AgI ($\Delta V=0.083$ val. un.)

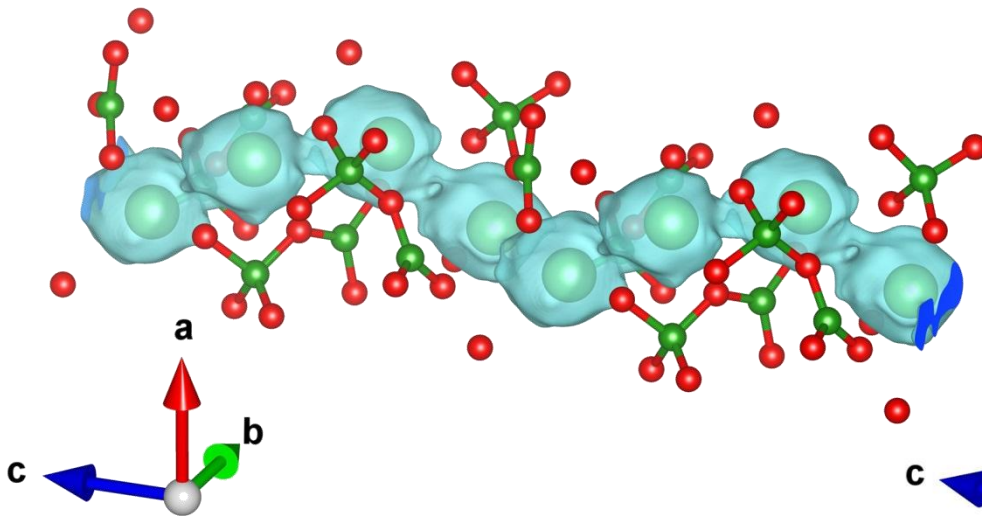
S. Adams, J. Swenson, Phys. Rev. B 63 (2000) 054201

Examples of the BVS isosurfaces

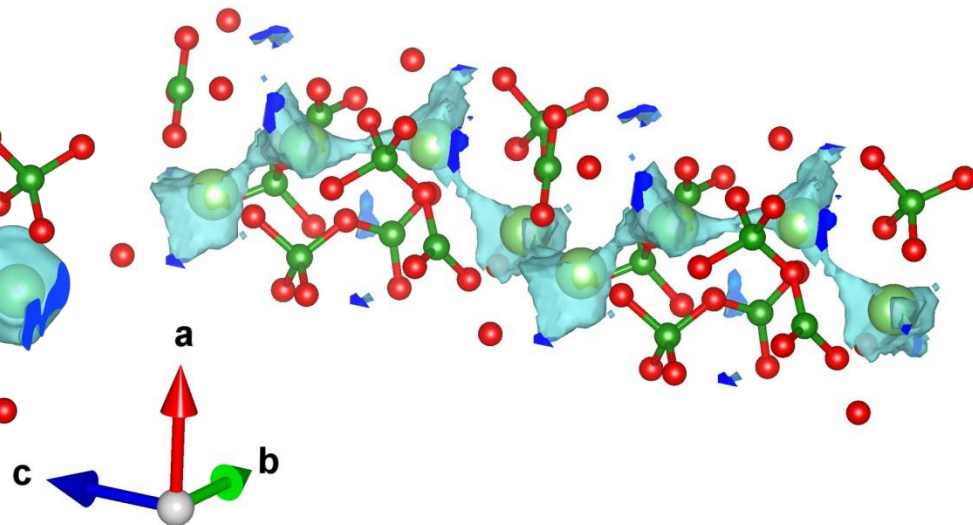
Differential bond-valence mismatch in $\text{Li}_2\text{B}_4\text{O}_7$

$$v_{\text{Li}-\text{O}} = \exp\left(\frac{1.17096\text{\AA} - R_{\text{Li}-\text{O}}}{0.516\text{\AA}}\right), R_{\text{cut}} = 5.5\text{\AA}$$

MEM reconstruction of negative (Li) nuclear scattering densities in $\text{Li}_2\text{B}_4\text{O}_7$



Differential valence map of lithium in $\text{Li}_2\text{B}_4\text{O}_7$ ($\Delta V = 0.2$ val. un.)



Ionic conduction and the BVS method

Limitation of the conventional BVS:

Only the first coordination shell is considered.

No energy units are available to compare between different compounds

Trick:

Use simple parameters for converting to an adequate potential allowing to get more precise results

Ionic conduction and the BVS method

Struct Bond (2014) 158: 129–160

DOI: 10.1007/430_2013_137

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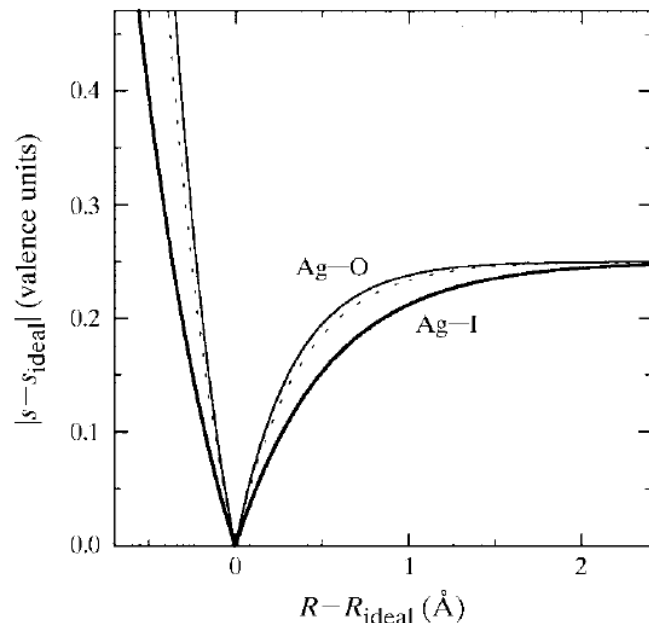
Understanding Ionic Conduction and Energy Storage Materials with Bond-Valence-Based Methods

Stefan Adams and R.Prasada Rao

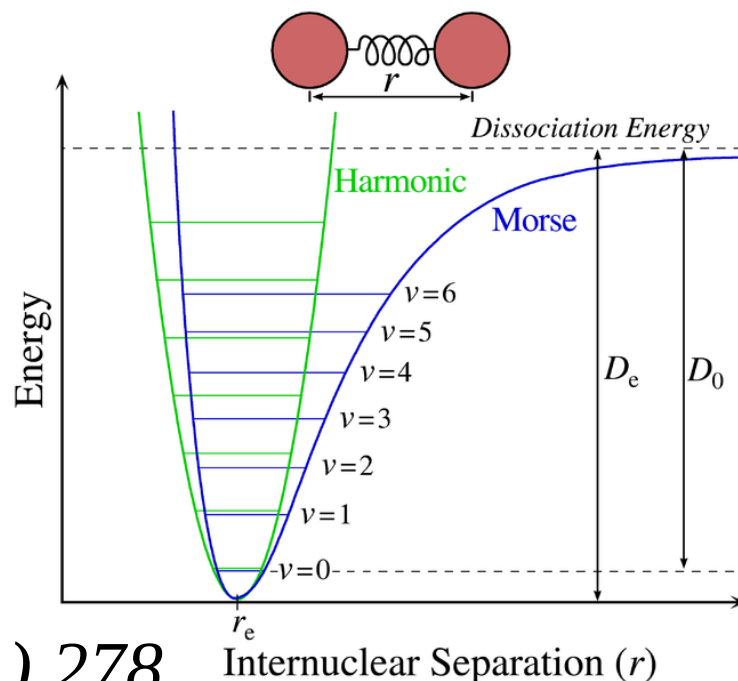
Extension of the BVS method

- Not only first coordination shell but a sphere with cutoff radius R_{cut} is considered;
- both R_0 and b parameters are adapted using bond-stiffness approach;

Pseudopotential representation of the correlation between bond-length R and bond valence s .



Typical Morse potential



Extension of the BVS method

Stefan Adams, *Practical Considerations in Determining Bond-Valence Parameters, Structure and Bonding* **158**, 91-128 (2014)

$$E = D_0 \left\{ (\exp[\alpha(R_{\min} - R)] - 1)^2 - 1 \right\}$$

$$= D_0 \left\{ \left(\frac{\exp\left[\frac{R_0 - R}{b}\right] - s_{\min}}{s_{\min}} \right)^2 - 1 \right\}$$

$$D_0 = \frac{kb^2}{2} = c \cdot 14.4 \frac{\text{eV}}{\text{\AA}} \frac{[V_{\text{id}}(\text{M}) \cdot V_{\text{id}}(\text{X})]^{1/c} b^2}{2R_{\min} \sqrt{n_{\text{M}} n_{\text{X}}}}, \quad R_{\min} \approx R_0 \times [f_1 + f_2 \cdot |\sigma_{\text{A}} - \sigma_{\text{X}}|] - b \cdot \ln\left(\frac{V_{\text{id}}}{N_{\text{C}}}\right).$$

$$\text{BVSE}(\text{M}) = D_0 \left[\sum_{j=1}^{N_{\text{X}}} \frac{(s_{\text{M-X}_j} - s_{\min})^2}{s_{\min}^2} - N \right] + \sum_{i=1}^{N_{\text{M}}} E_{\text{Coulomb}}(\text{M} - \text{M}_i)$$

$$E_{\text{Coulomb}}(\text{M}_1 - \text{M}_2) = \frac{q_{\text{M}_1} q_{\text{M}_2}}{R_{\text{M}_1 - \text{M}_2}} \text{erfc}\left(\frac{R_{\text{M}_1 - \text{M}_2}}{\rho_{\text{M}_1 - \text{M}_2}}\right)$$

Extension of the BVS method

computer programs

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**3DBVSMAPPER: a program for automatically
generating bond-valence sum landscapes**

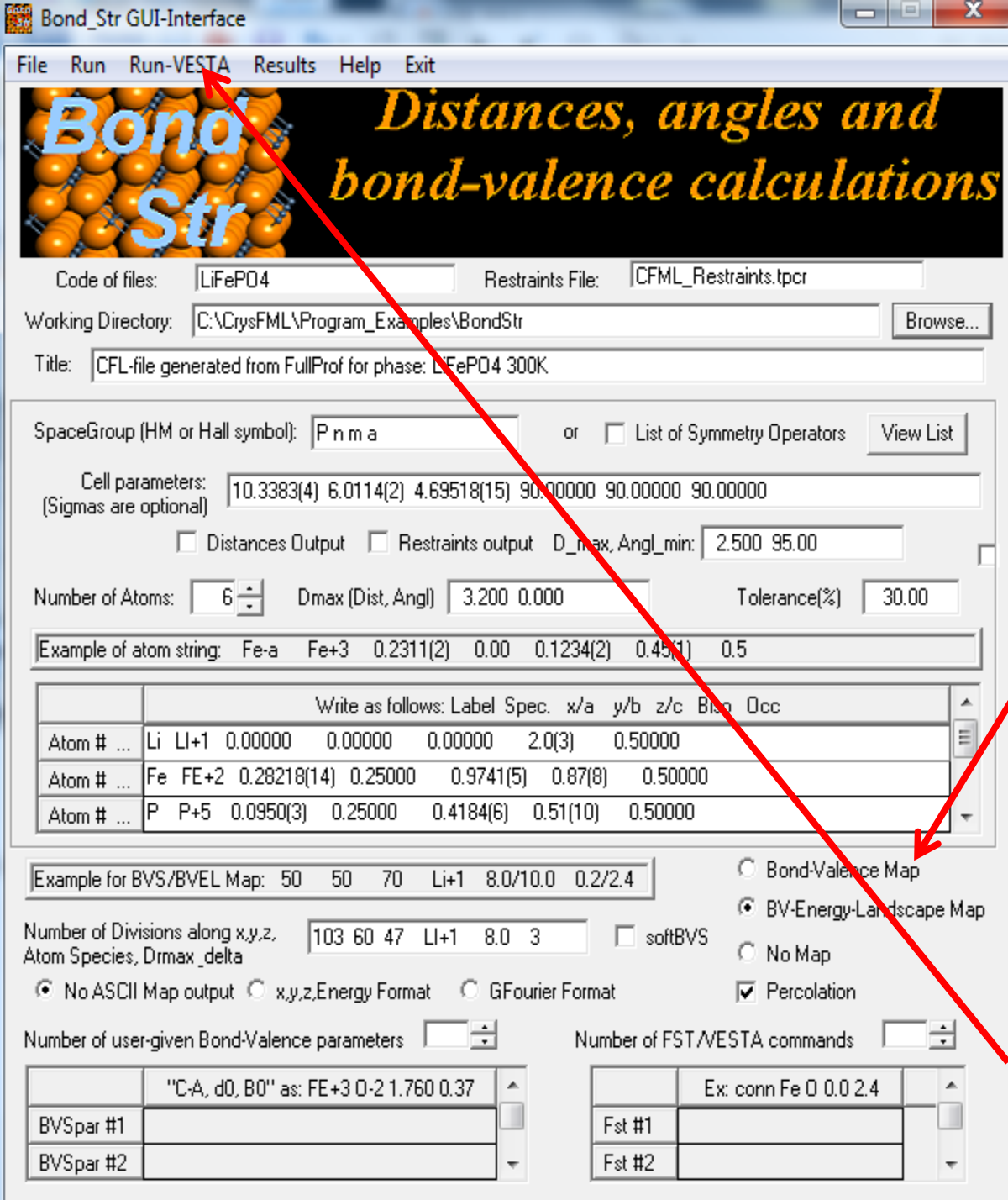
Matthew Sale* and Maxim Avdeev*

$$\text{BVEL}_{+/-} = \sum_{j=1}^N \left(m_j D_0 \{ \exp[\alpha(R_{\min} - d_j)] - 1 \}^2 - 1 \right), \quad (2)$$

$$\begin{aligned} \text{BVEL}_{+/+, -/-} = \sum_{j=1}^N \left\{ \text{ConvEV} \frac{m_j}{d_j} \frac{|V_{\text{TI}}| |V_j|}{(n_{\text{qnTI}} n_{\text{qnj}})^{1/2}} \right. \\ \left. \times \left[\text{erfc}\left(\frac{d_j}{\hat{a}}\right) - \text{erfc}\left(\frac{d_{\text{cutoff}}}{\hat{a}}\right) \right] \right\}, \quad (3) \end{aligned}$$

The program needs the use of Materials Studio

$$\rho = \rho_{\text{f}}(r_{\text{TI}} + r_j), \quad (4)$$



NEW options

Now in **Bond_Str** there is the **possibility** to calculate bond-valence energy landscapes (BVEL) (see fp2k.inf, note of 16 January 2015)

The BVEL isosurfaces can be visualized using VESTA

Output of Bond_Str

====>

Calculation of Bond-Valence Energy Landscape Map

Bond-Valence Energy parameters (D0,Rmin,alpha) for Morse Potential: $D0 * [\exp(\alpha(d_{min}-d)) - 1]^2$
(data read from internal table, provided by the user or calculated from softBVS parameters)

Type 1: FE+2 with type 4: O-2

D0 = 1.69269 Rmin = 1.96005 Alpha = 2.08333
Av. Coord.= 5.74300 R0 = 1.57911 R-cutoff = 5.50000 => Reference: S. Adams and R. Pra
Cation (Eff. radius): FE+2(1.260) Anion (Eff. radius): O-2 (1.330)

Type 2: LI+1 with type 4: O-2

D0 = 0.98816 Rmin = 1.94001 Alpha = 1.93798
Av. Coord.= 5.02100 R0 = 1.17096 R-cutoff = 5.50000 => Reference: S. Adams and R. Pra
Cation (Eff. radius): LI+1(1.310) Anion (Eff. radius): O-2 (1.330)

Type 3: P+5 with type 4: O-2

D0 = 3.89635 Rmin = 1.44066 Alpha = 2.28833
Av. Coord.= 4.00000 R0 = 1.62038 R-cutoff = 5.00000 => Reference: S. Adams and R. Pra
Cation (Eff. radius): P+5 (1.100) Anion (Eff. radius): O-2 (1.330)

=> Global distance cutoff: 8.0000 angstroms

Output of Bond_Str

====>

```
=> Value of Delta (for volume calculation) :    3.0000 eV
=> Available volume for ion mobility in the unit cell:    30.0735 angstroms^3
=> Volume fraction for ion mobility in the unit cell:    10.31 %
=> Minum Energy (in eV):    -4.5907
=> Number of pixels with Emin < Energy < Emin+Delta:    29936

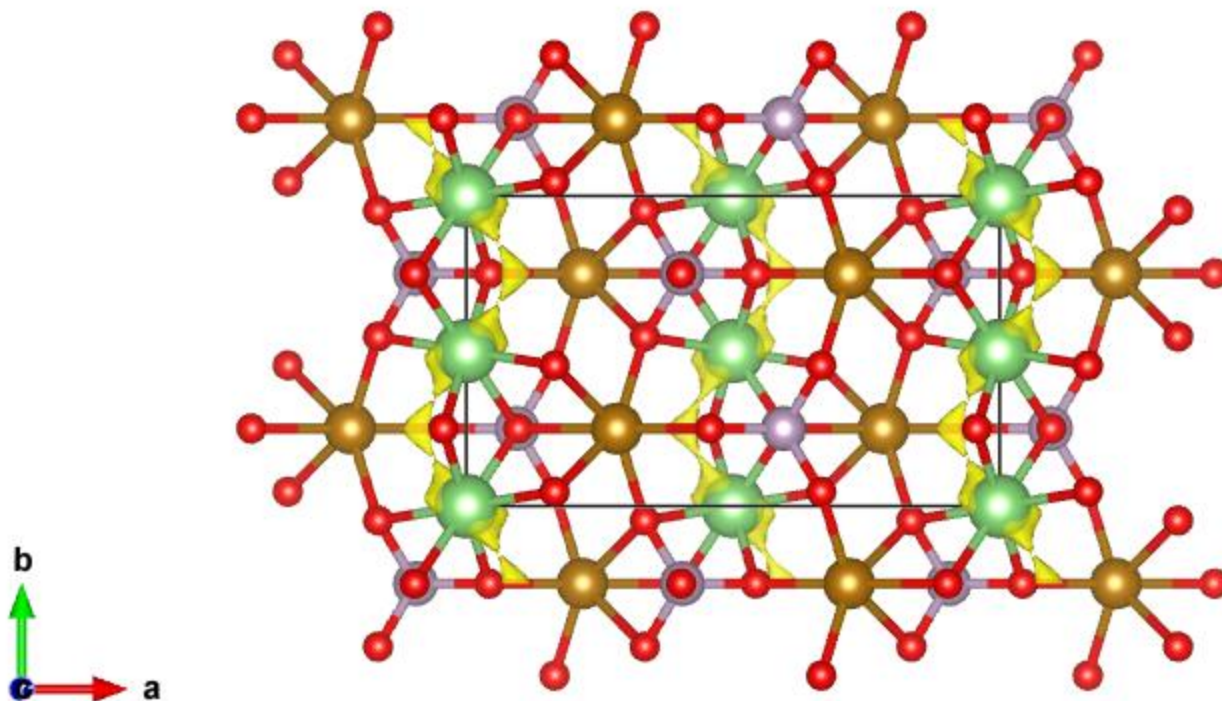
=> Computing first estimation of percolation energies (it can take some minutes) ....
Percolation along a: No
Percolation along b: Yes, Percolation energy:    1.00 eV
Percolation along c: No

=> Refining energies....
axis b
    Searching percolation between    0.50 and    1.01 eV
        Percolation energy above Emin:    0.90 eV
    Searching percolation between    0.80 and    0.91 eV
        Percolation energy above Emin:    0.88 eV,    Isosurface for VESTA:    -3.71 eV

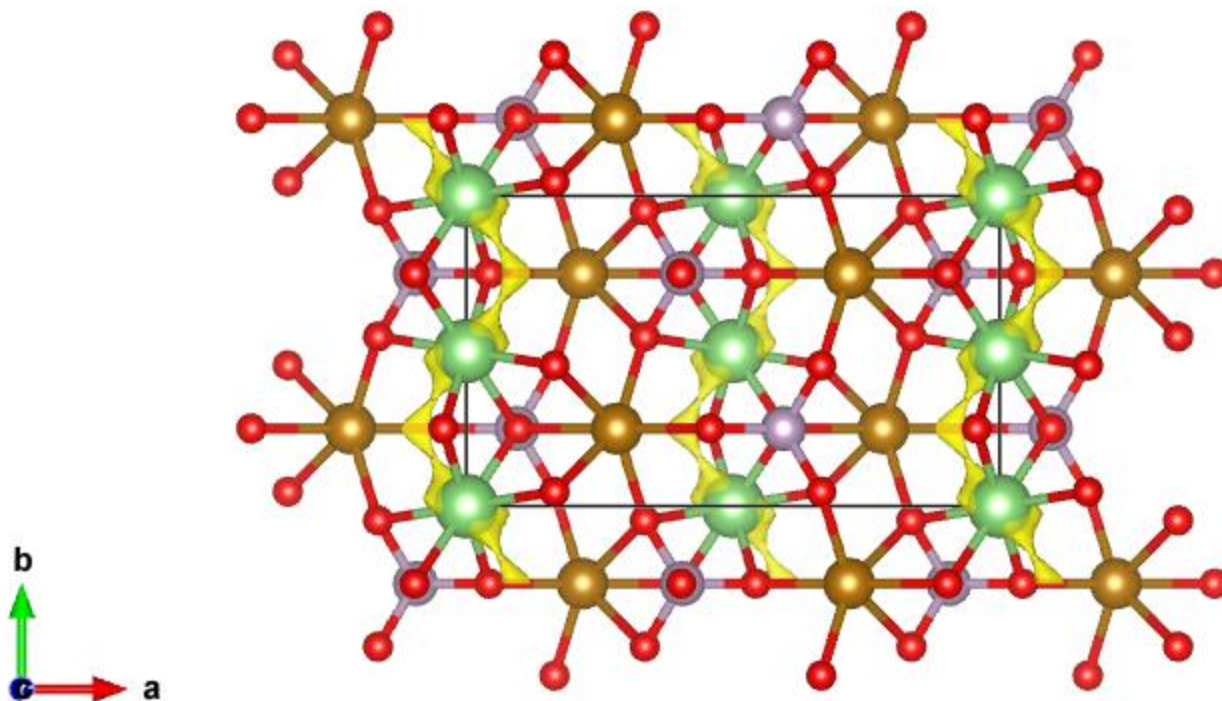
=> Bond Valence Energy Landscape in File: LiFePO4_bvel.map
=> VESTA File: LiFePO4_str.vesta

=> Normal End of: PROGRAM BOND_STR
=> CPU-time:    12.9949 seconds
* * * End of File * * *
```

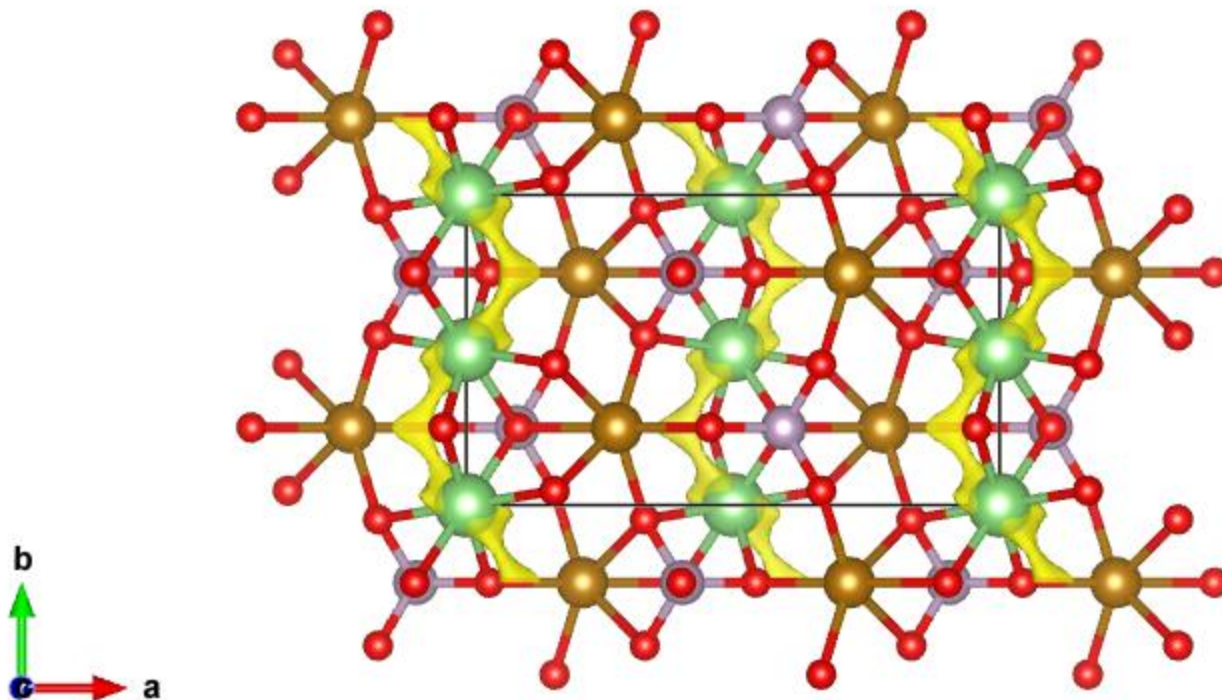
Iso-surface at the percolation energy: -3.71 eV



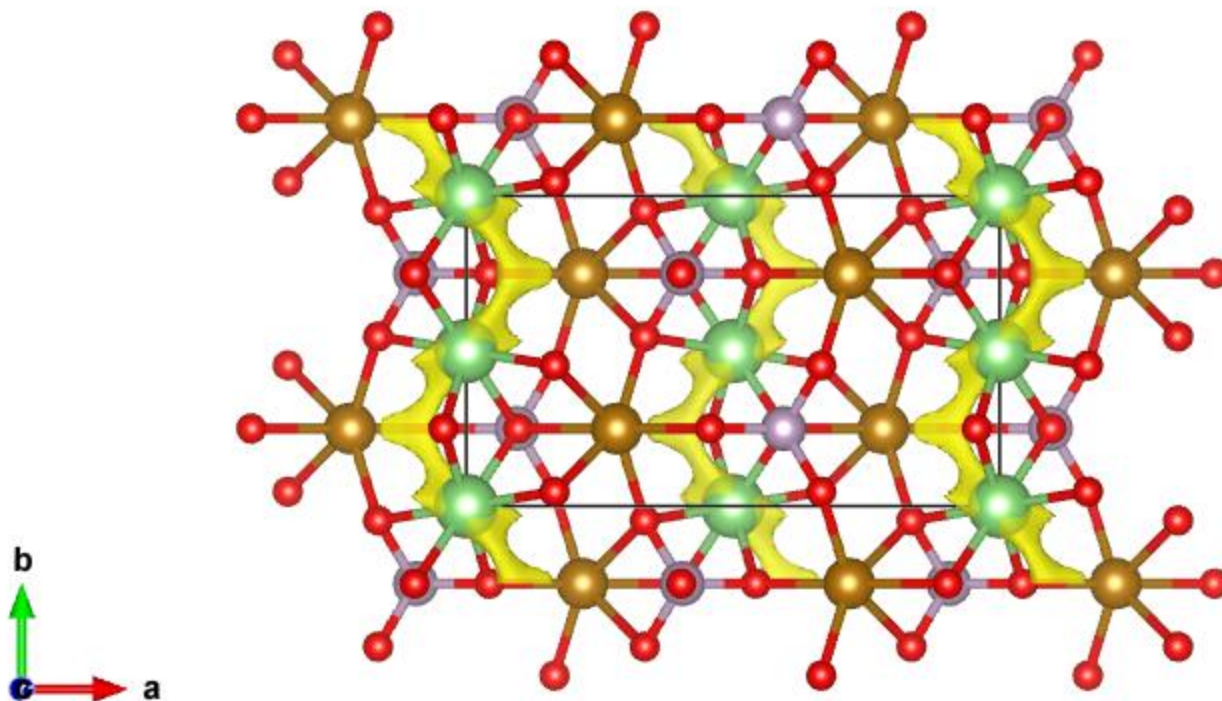
Iso-surface at energy: -3.69 eV



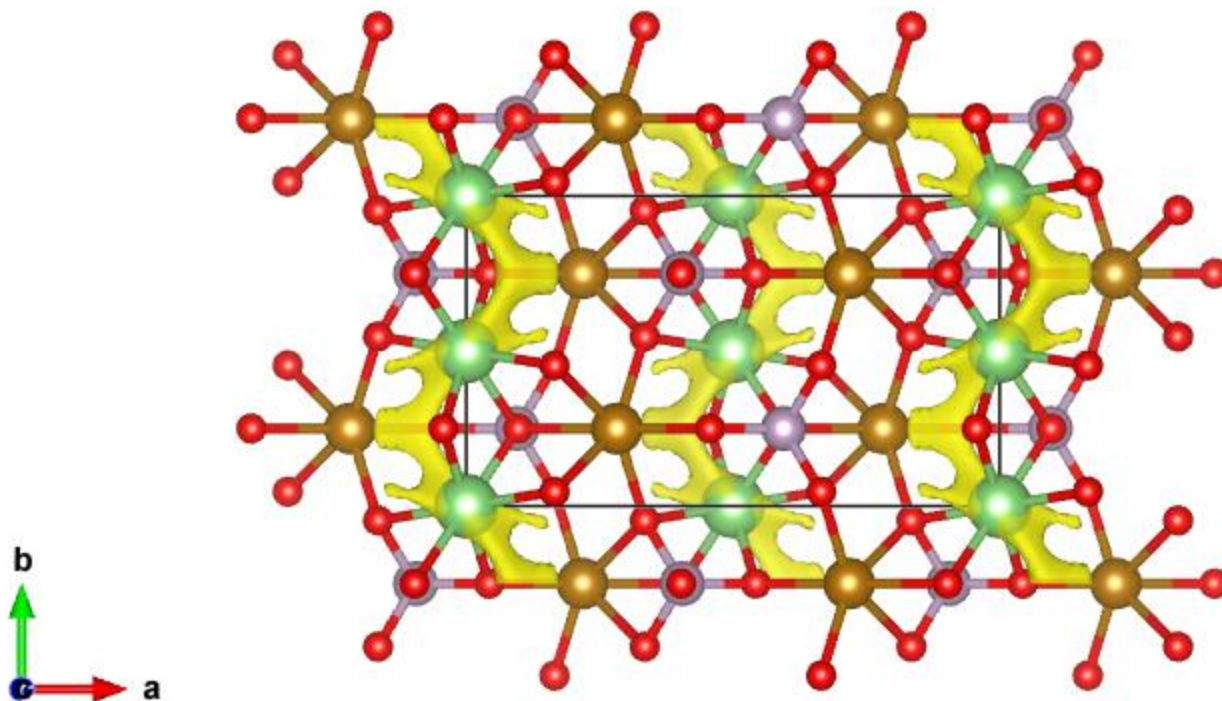
Iso-surface at energy: -3.60 eV



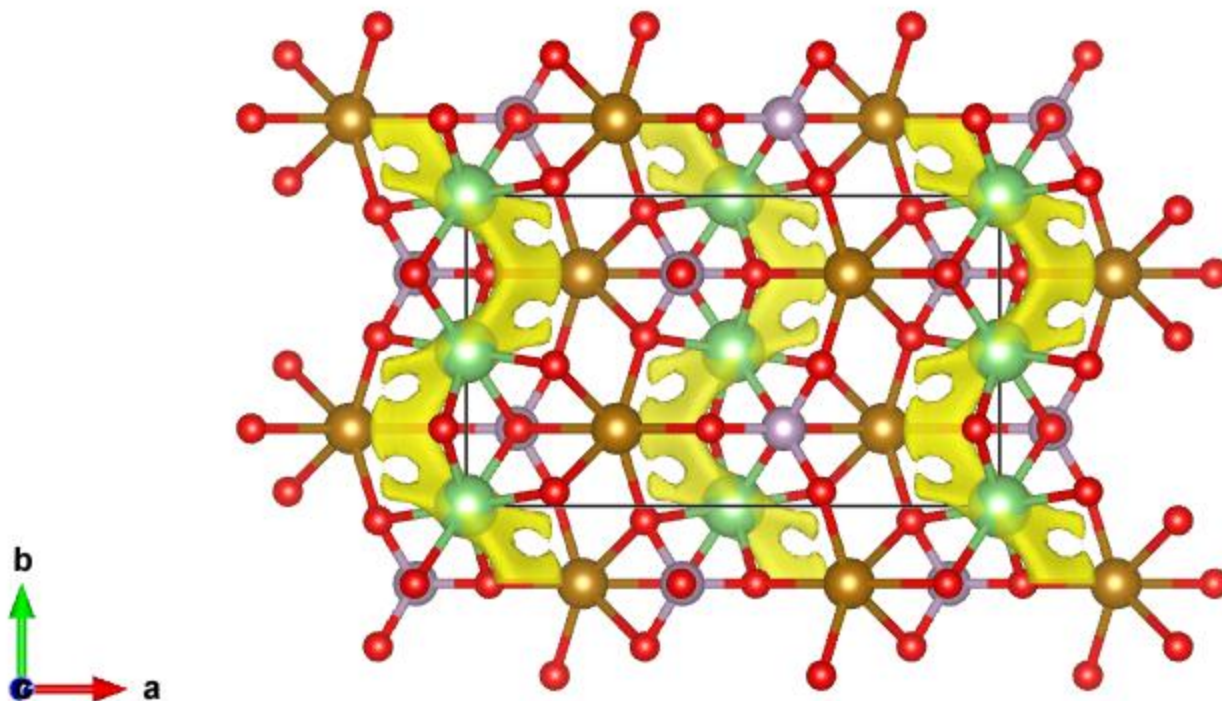
Iso-surface at energy: -3.50 eV



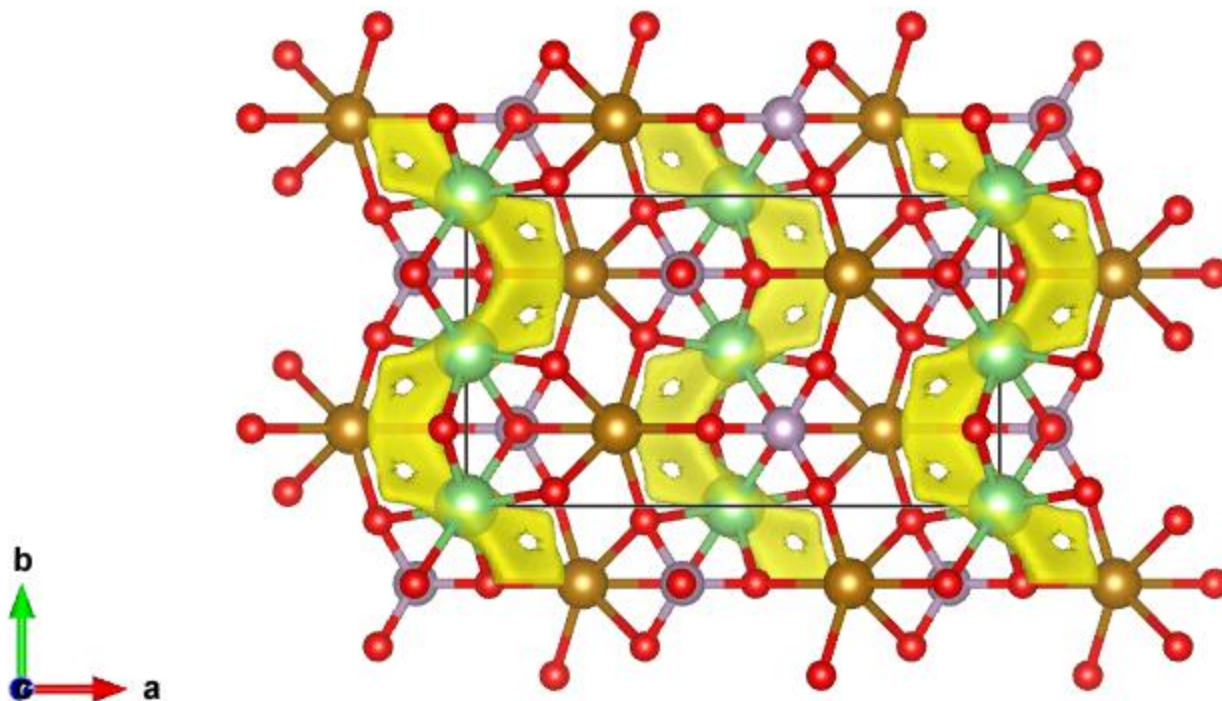
Iso-surface at energy: -3.40 eV



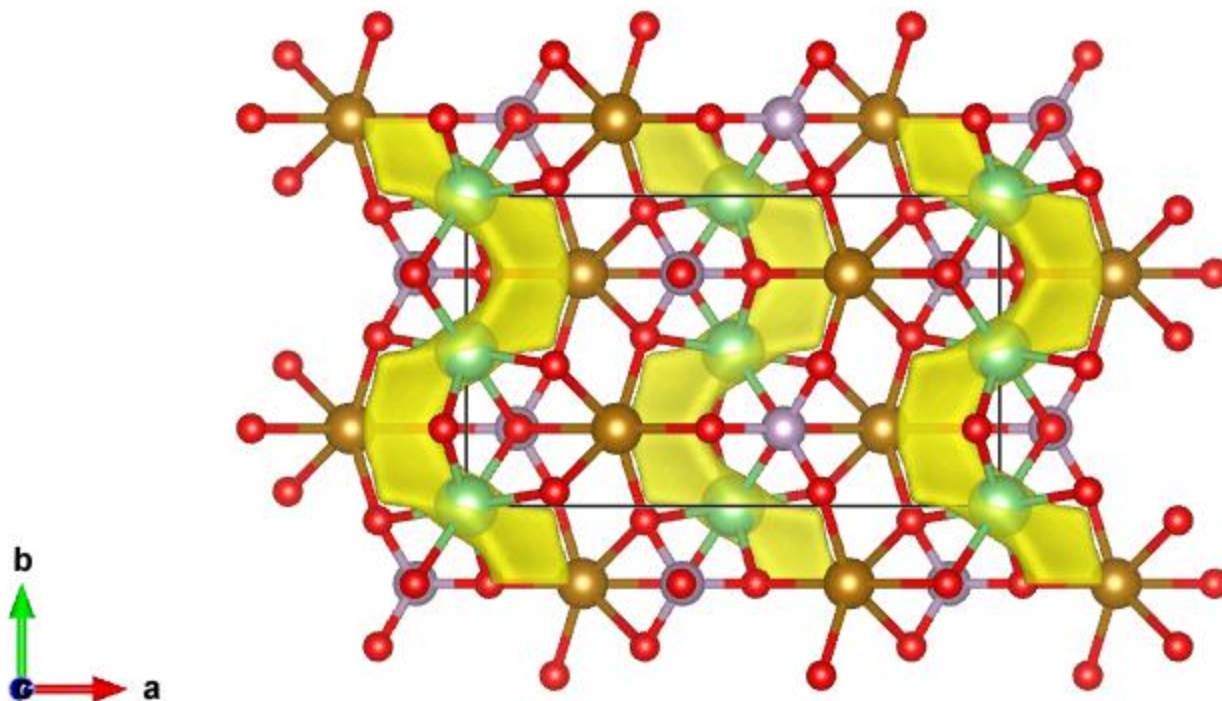
Iso-surface at energy: -3.30 eV



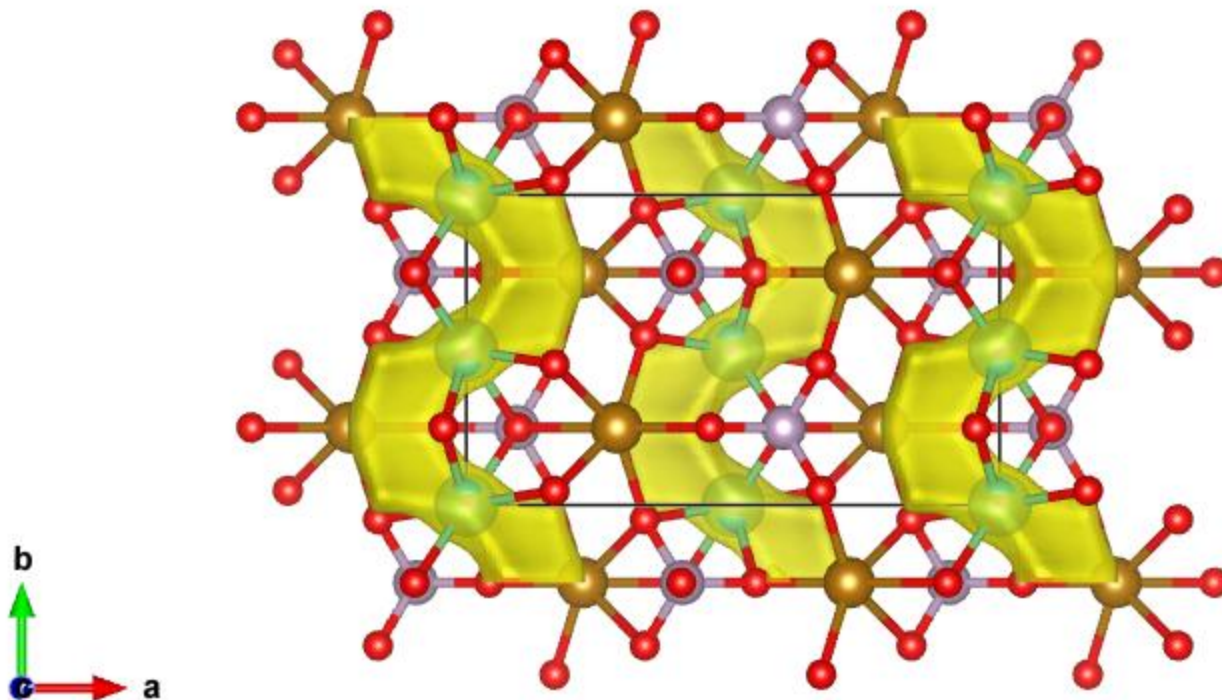
Iso-surface at energy: -3.20 eV



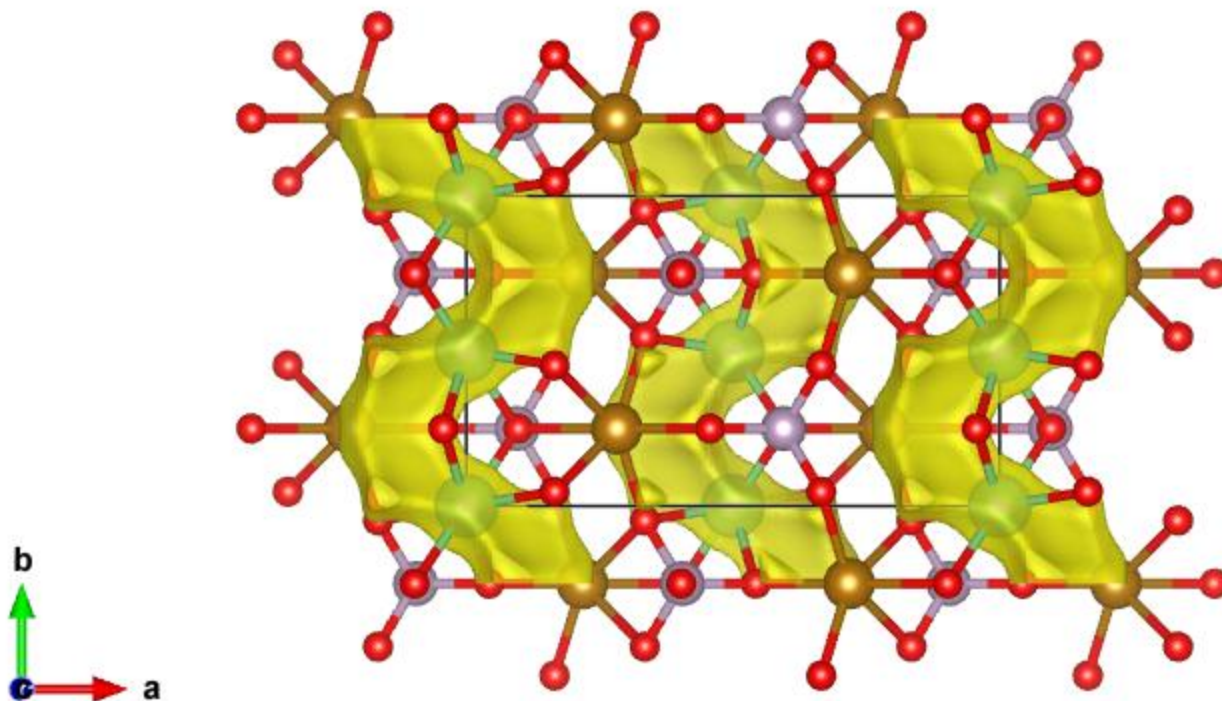
Iso-surface at energy: -3.00 eV



Iso-surface at energy: -2.00 eV



Iso-surface at energy: -1.00 eV

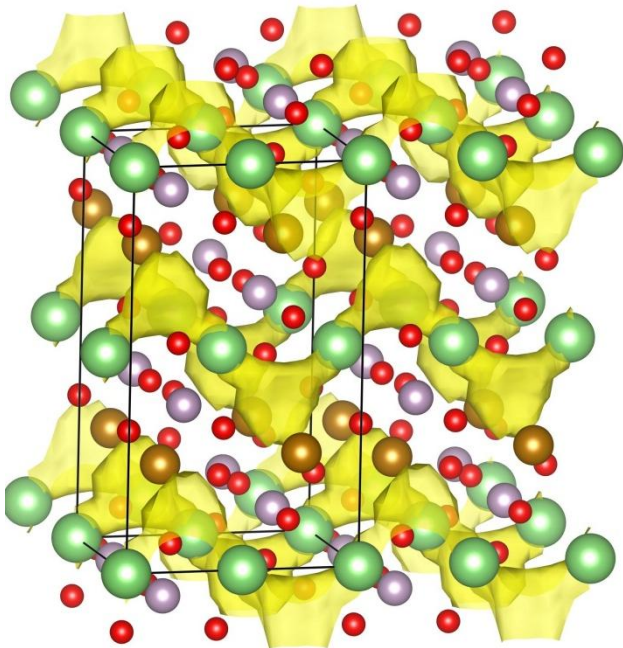


Examples of the BVEL isosurfaces

Cathodes for Li-ion batteries

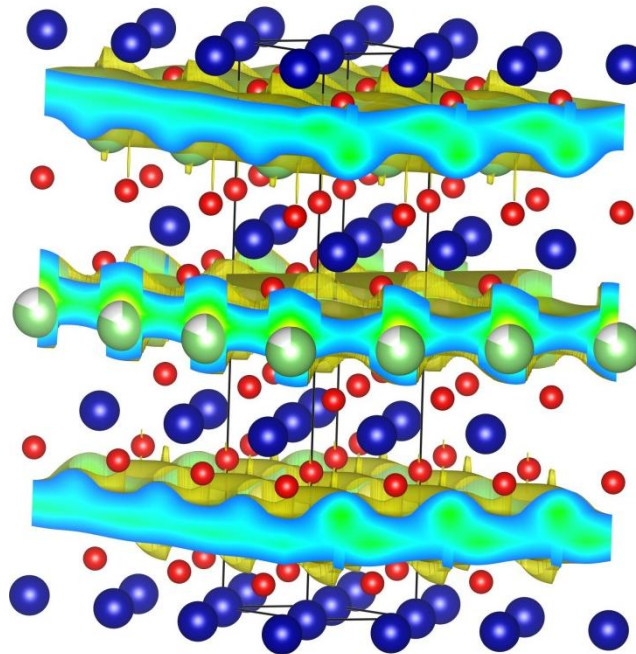
1D

Li_xFePO_4
olivine



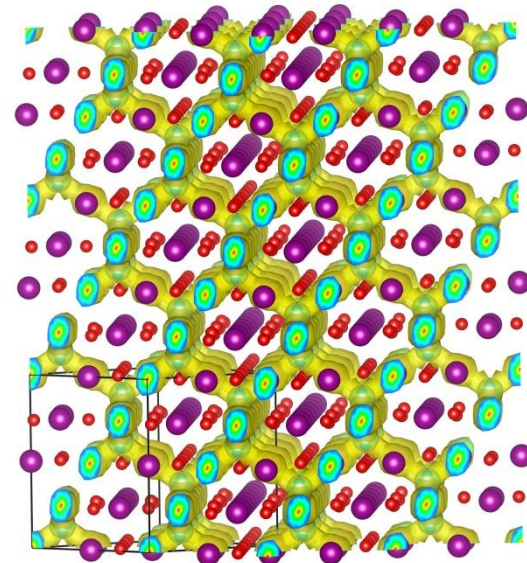
2D

Li_xCoO_2
distorted rock-salt



3D

LiMn_2O_4
spinel



Examples of the BVEL isosurfaces

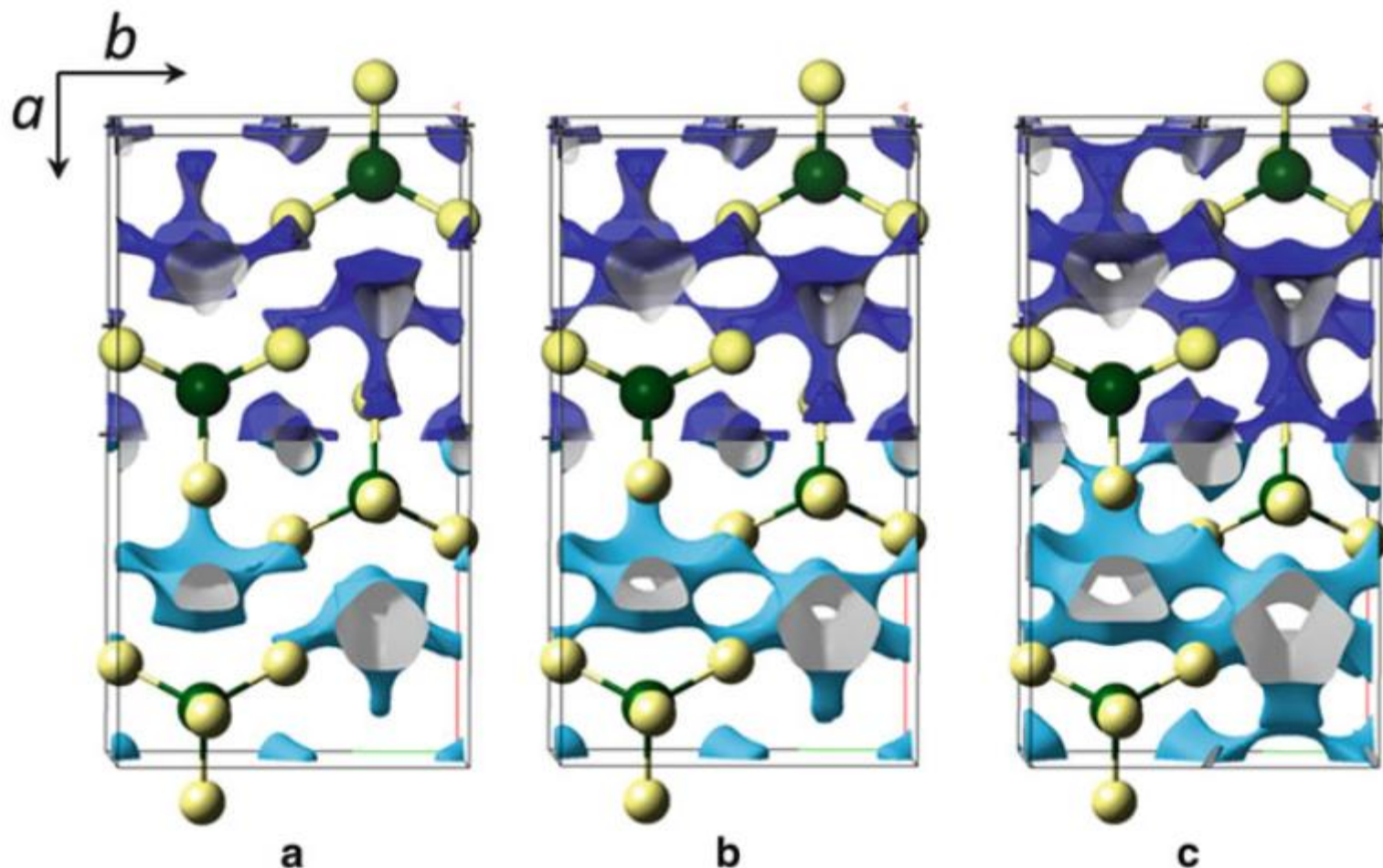


Fig. 12 Regions in the Li_4GeS_4 structure accessible to moving Li^+ ions according to BVSE energy calculations (*top half* of the unit cell) for ΔE_{BVSE} of (a) 0.95 eV, (b) 1.1 eV and (c) 1.35 eV and the procrystal analysis (*bottom half* of the unit cell) showing paths with electron density isovalues of 0.0016 au, 0.0018 au, and 0.0024 au, respectively

Summary

- Bond-Valence Energy maps/isosurfaces give a clear evidence (first approximation) for the ionic diffusion pathways in the material
- BVEL Model has a high predictive potential and is adapted for studying whatever ionic diffusion species
 - the cation conductors, e.g. sodium or magnesium
 - the anion conductors, e.g. oxygen or hydrogen ...
 - This model is now used to predict percolation energies and conduction paths systematically on databases (i.e. ICSD)
- The BVEL Model is restricted to compounds close to ionic character; e.g. it does not, in general, apply to metals or organic compounds
- The program **Bond_Str** together with a GUI is distributed within the **FullProf Suite**. The source code is freely available within the repository of the CrysFML library:

<https://forge.epn-campus.eu/projects/crysfml/repository>

Some representative references

Long-range Coulomb forces and localized bonds

Christoph Preiser, Jens Loesel, I. David Brown, Martin Kunz and Aniceta Skowron
Acta Cryst. **B55**, 698-711 (1999)

Recent Developments in the Methods and Applications of the Bond Valence Model

Ian David Brown

Chem. Rev. **109**, 6858–6919 (2009)

High power lithium ion battery materials by computational design

Stefan Adams and R. Prasada Rao

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Matthew Sale and Maxim Avdeev,

Journal of Applied Crystallography **45**, 1054–1056 (2012)

Practical Considerations in Determining Bond Valence Parameters

Stefan Adams

Structure and Bonding **158**, 91–128 (2014)

Understanding Ionic Conduction and Energy Storage Materials with Bond-Valence-Based Methods

Stefan Adams and R. Prasada Rao

Structure and Bonding **158**, 91–128 (2014)