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

The Program Bond_Str

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J. Appl. Cryst. (2019). **52**, 148–157

Appl Cryst JAC JOURNAL OF APPLIED CRYSTALLOGRAPHY

ISSN 1600-5767

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 (≈ 0.37Å) are tabulated parameters characteristic of the pair *A*-*X* and $R_{A\text{-}X}$ 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):

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

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

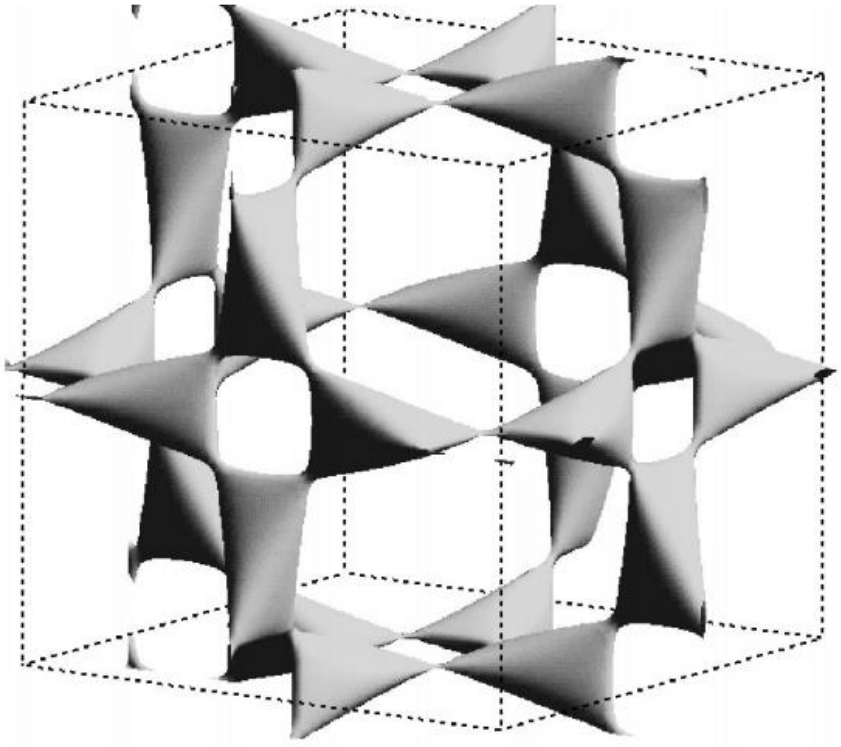
The bond-valence method can be used for assessing the ionic conduction path from the knowledge of the crystal structure.

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

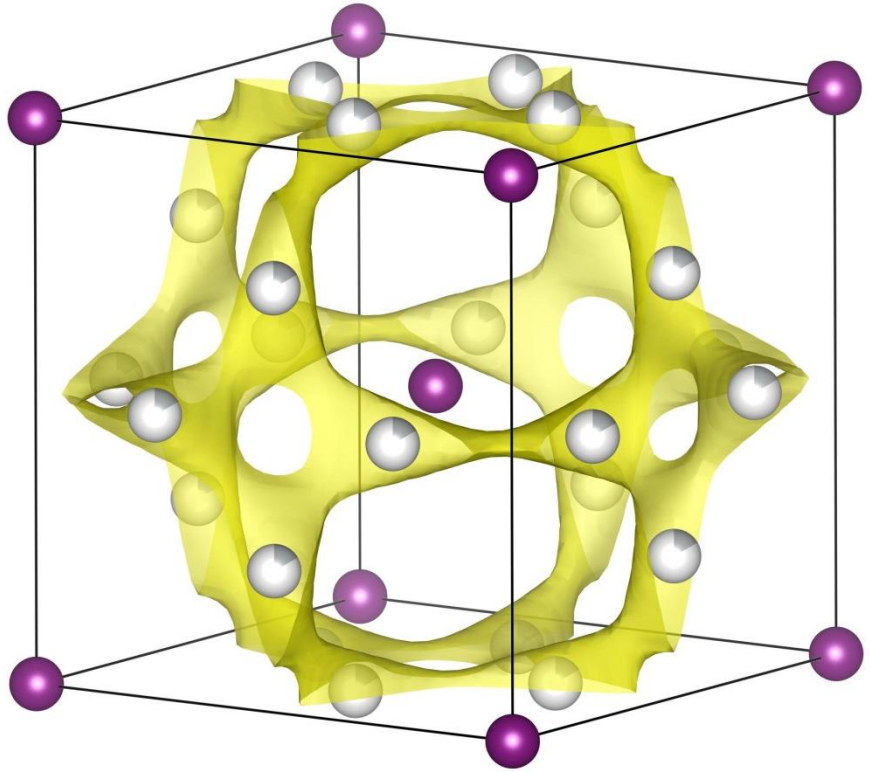
Examples of the BVS isosurfaces

Differential bond-valence mismatch in Ag-I

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



Bond valence isosurface for α-AgI (ΔV=0.05 val. un.)



Bond valence isosurface for α-AgI (ΔV=0.083 val. un.)

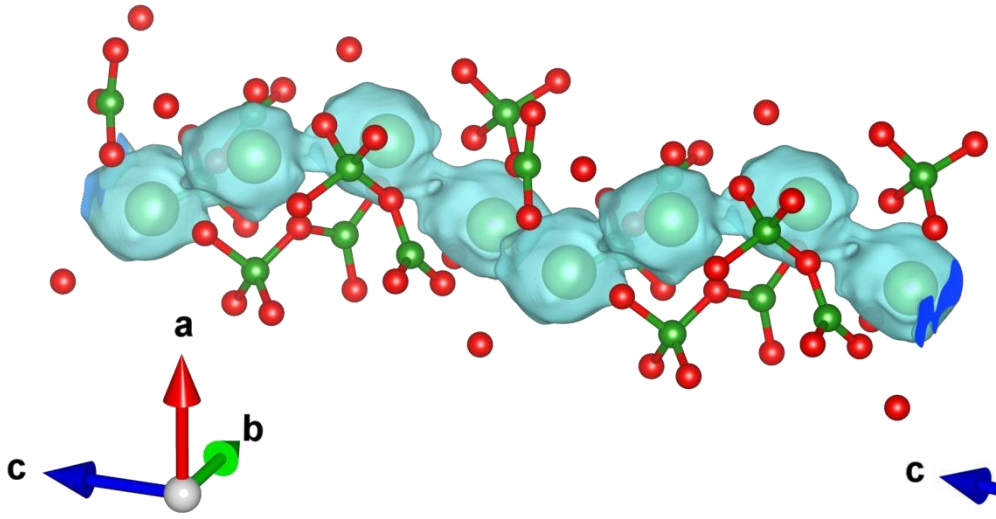
S. Adams, J. Swenson, Phys. Rev. B 63 (2000) 054201

Examples of the BVS isosurfaces

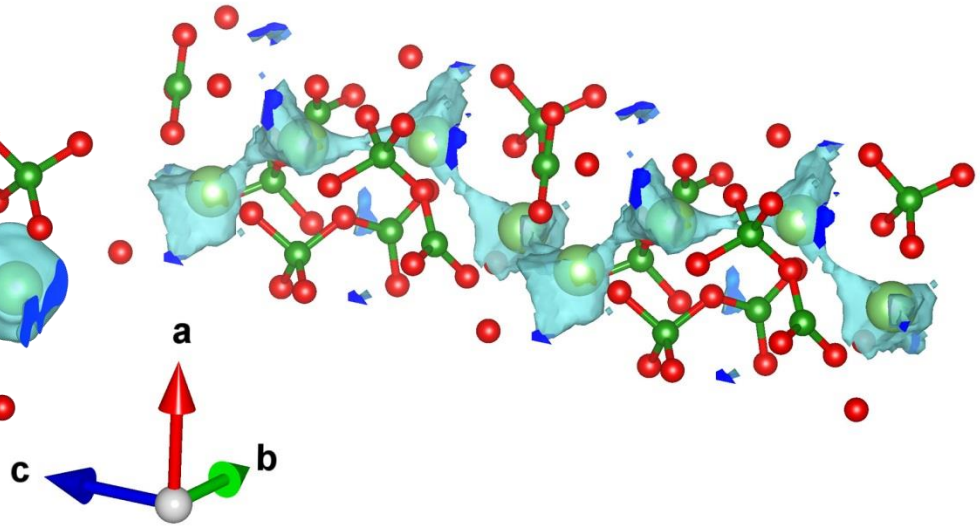
Differential bond-valence mismatch in $Li_2B_4O_7$

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

MEM reconstruction of negative (Li) nuclear scattering densities in $Li_2B_4O_7$



Differential valence map of lithium in $Li_2B_4O_7$ (ΔV=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

Published online: 12 February 2014

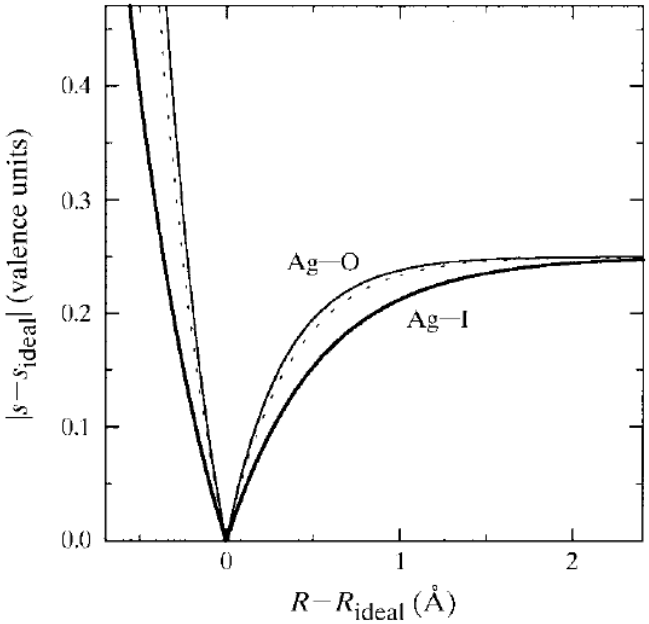
Understanding Ionic Conduction and Energy Storage Materials with Bond-Valence-Based Methods

Stefan Adams and R.Prasada Rao

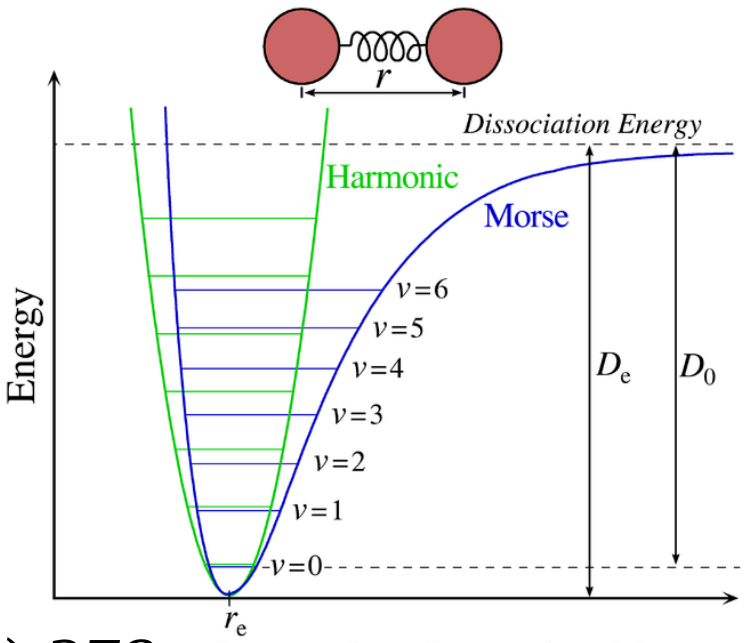
Extension of the BVS method

- 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-stifness approach;

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



Typical Morse potential



S. Adams, Acta Cryst. B 57 (2001) 278

Extension of the BVS method

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

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

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

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

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

Extension of the BVS method

computer programs

Journal of
Applied
Crystallography

ISSN 0021-8898

Received 8 March 2012
Accepted 20 July 2012

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

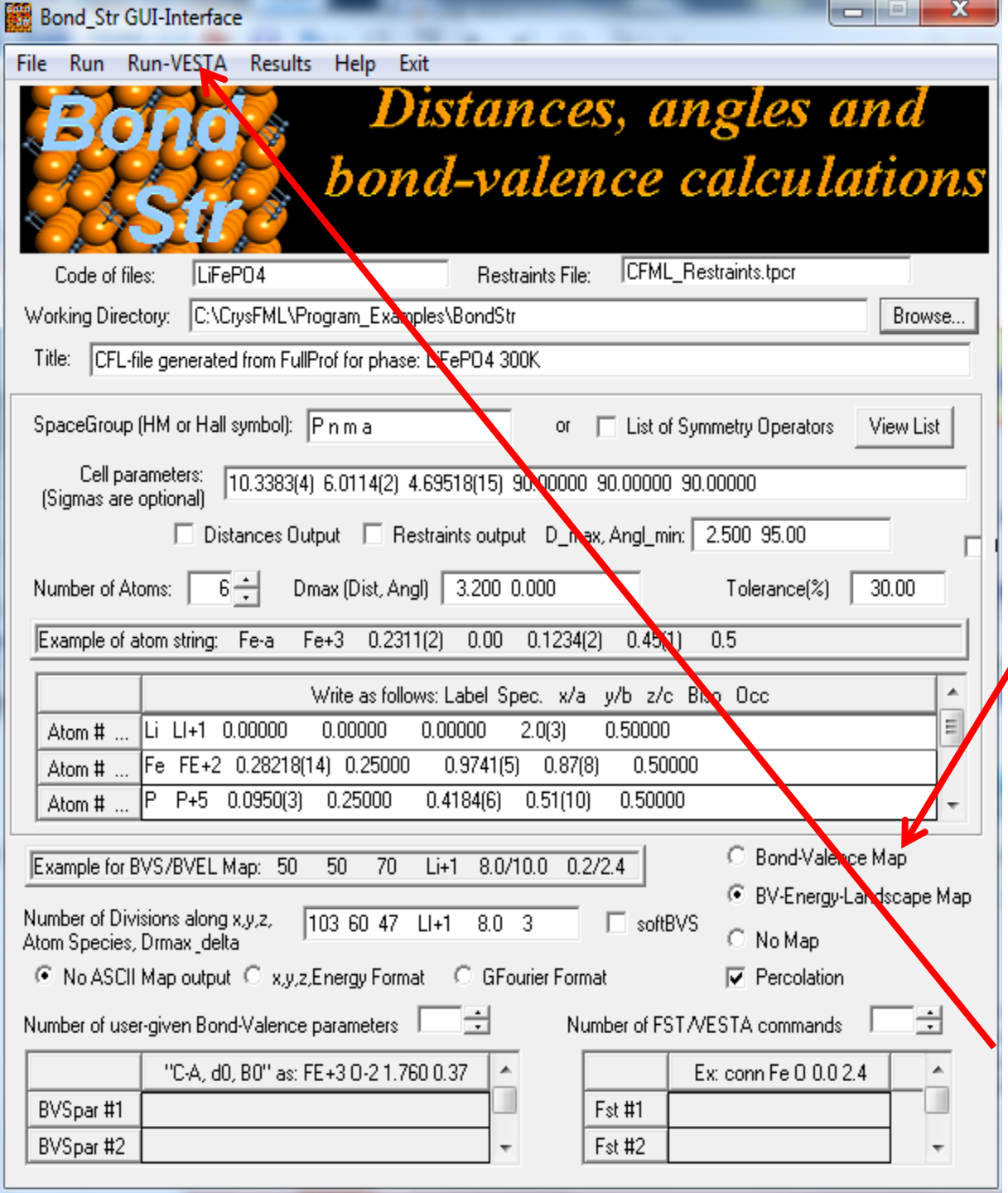
Matthew Sale* and Maxim Avdeev*

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

$$\mathrm{BVEL}_{+/+,-/-} = \sum_{j=1}^{N}\left\{\mathrm{ConvEV}\,\frac{m_j}{d_j}\,\frac{|V_{\mathrm{TI}}||V_j|}{\left(n_{\mathrm{qnTI}} n_{\mathrm{qn}j}\right)^{1/2}} \times \left[\mathrm{erfc}\left(\frac{d_j}{\quad}\right) - \mathrm{erfc}\left(\frac{d_{\mathrm{cutoff}}}{\quad}\right)\right]\right\}, \qquad (3)$$

The program needs the use of Materials Studio

$$\rho = \rho_{\mathrm{f}}\left(r_{\mathrm{TI}} + r_j\right), \qquad (4)$$



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

KEDIT - [C:\CrysFML\Program_Examples\BondStr\LiFePO4.bvs]

File Edit Actions Options Window Help

671.0

```
====>
    ------------------------------------------------
       Calculation of Bond-Valence Energy Landscape Map
    ------------------------------------------------


 Bond-Valence Energy parameters (D0,Rmin,alpha) for Morse Potential:  D0*[{exp(alpha(dmin-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
```

Line=148 Col=57 Alt=0,0;0 Size=182 Files=5 Windows=5 OVR R/W 02:27

KEDIT - [C:\CrysFML\Program_Examples\BondStr\LiFePO4.bvs]

File Edit Actions Options Window Help

671.0

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 * * *
```

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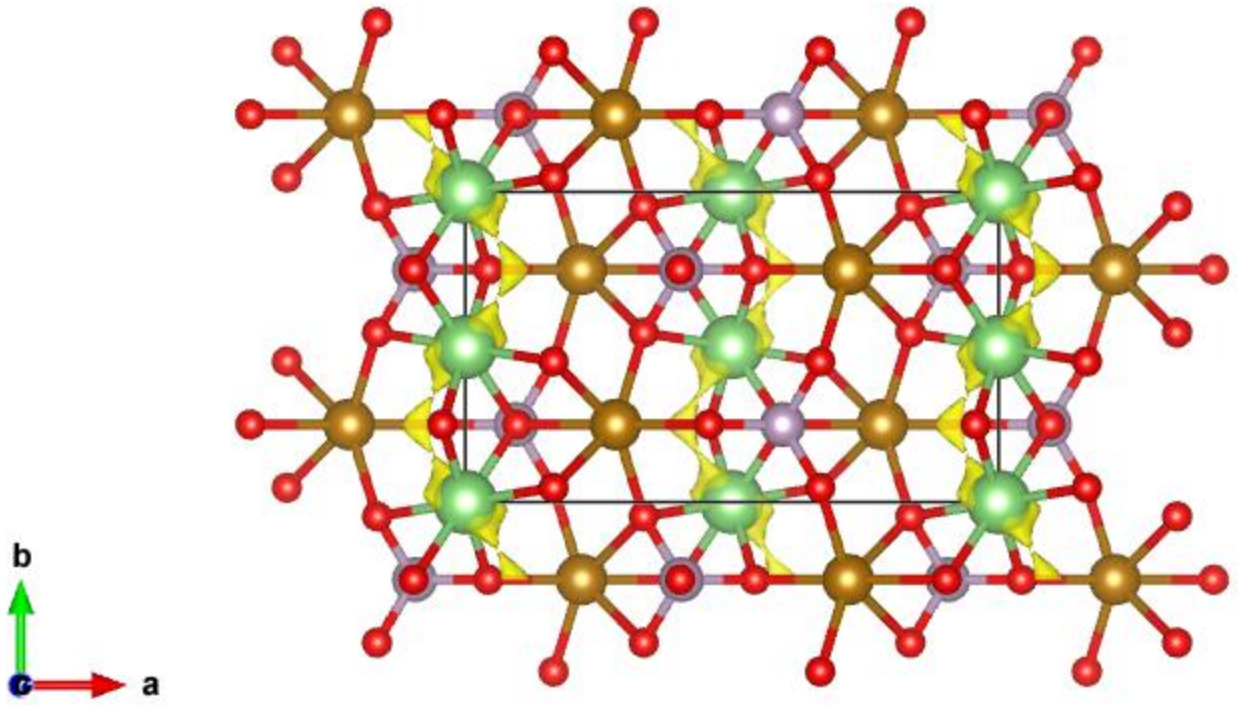
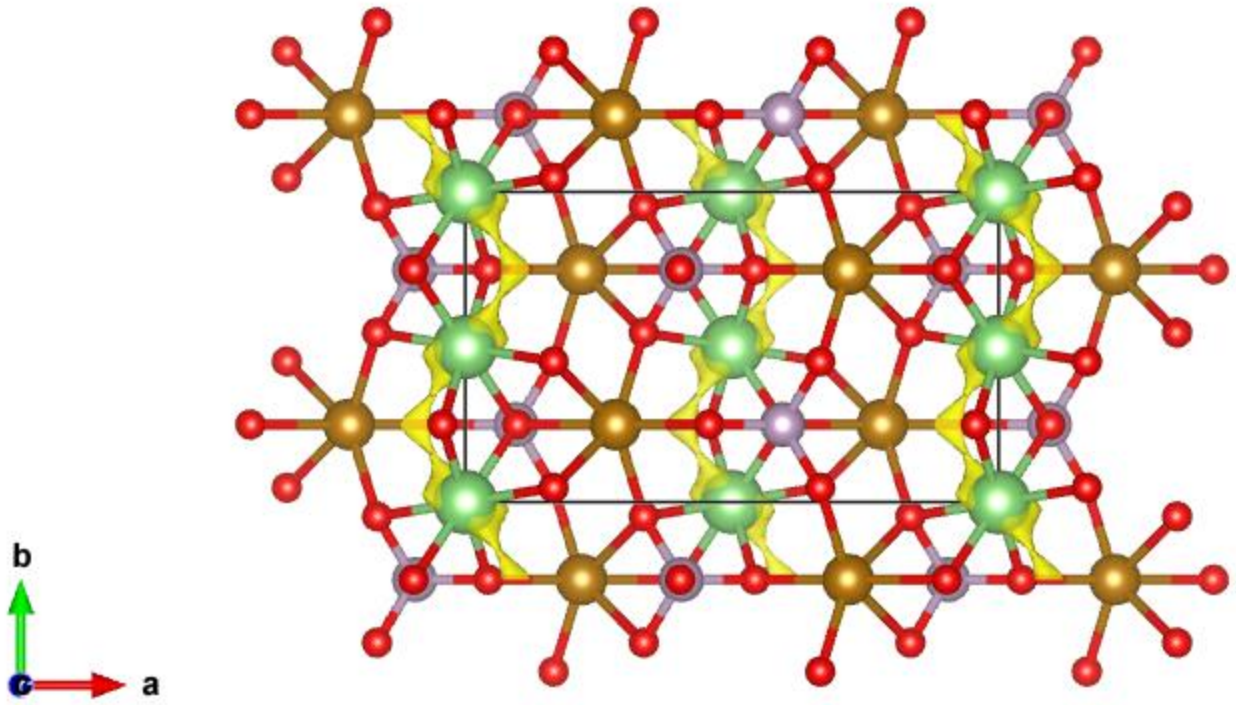
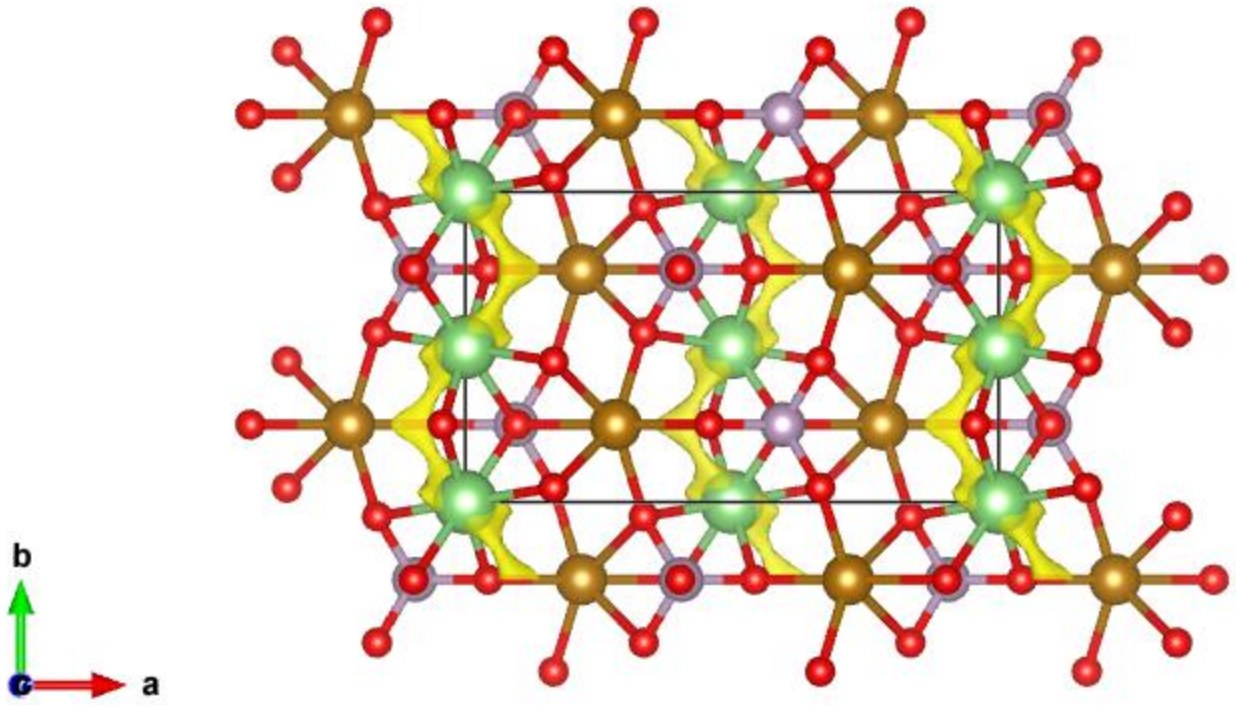
Iso-surface at the percolation energy: -3.71 eV



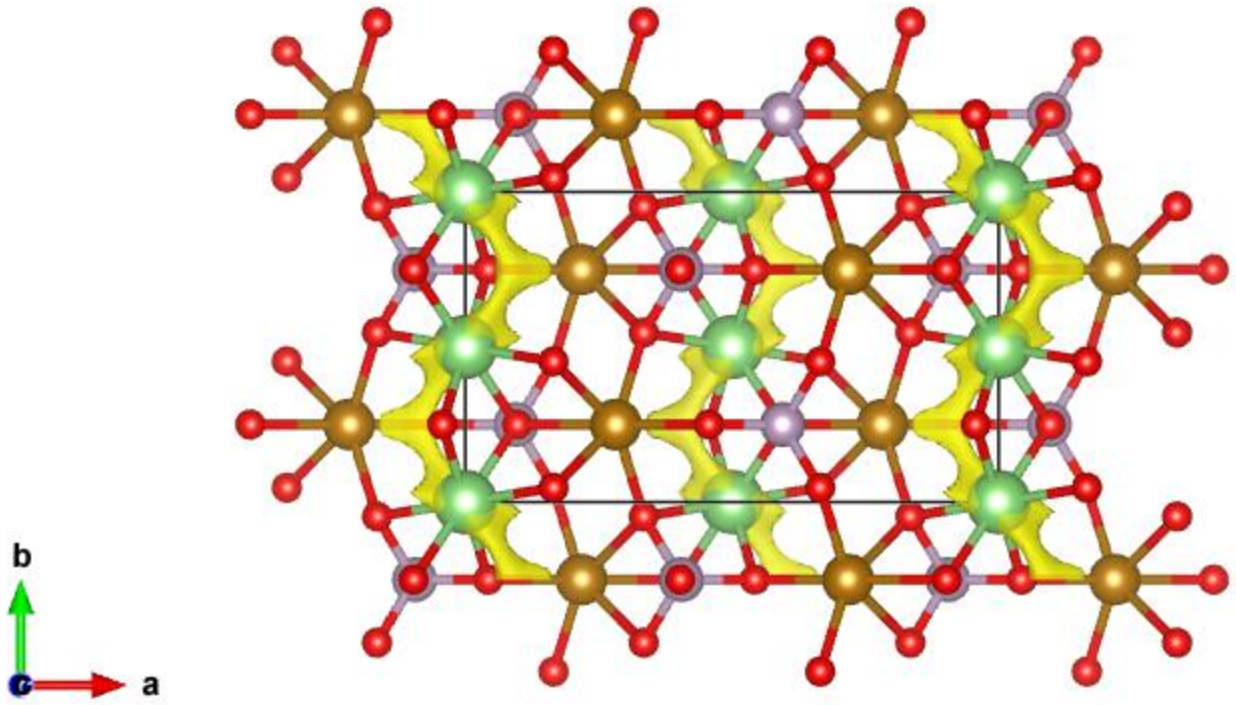
Iso-surface at energy: -3.69 eV



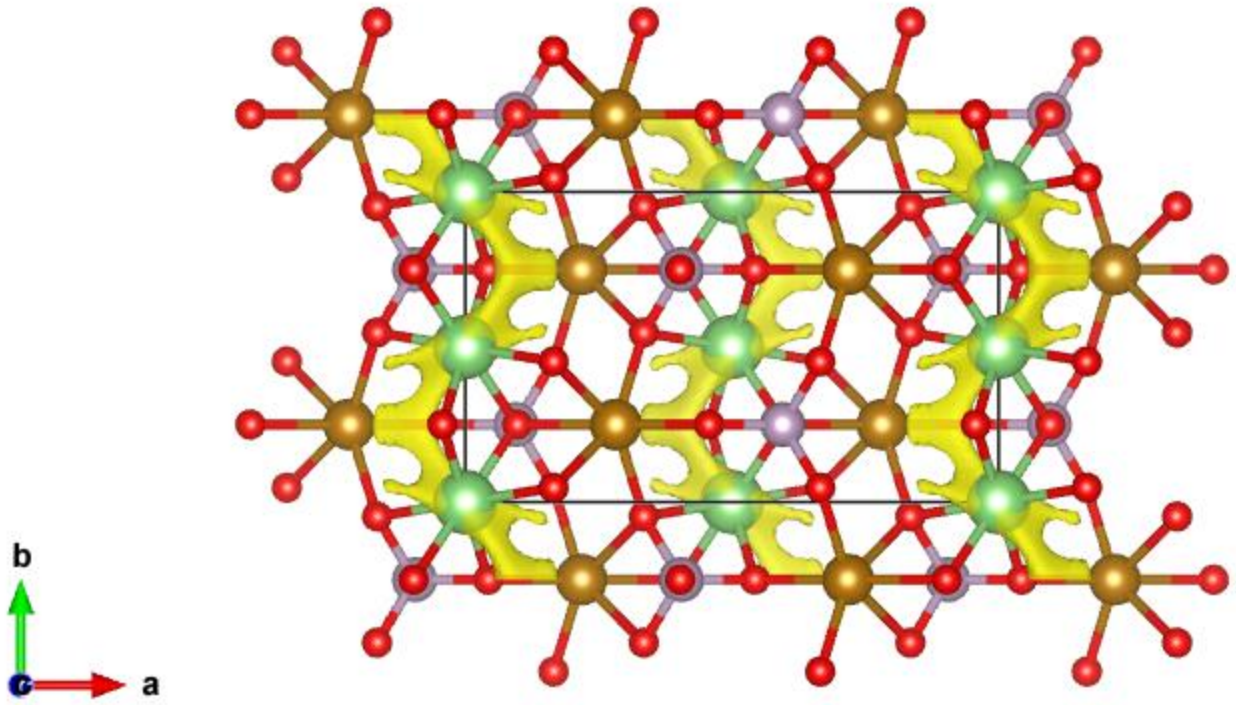
Iso-surface at energy: -3.60 eV



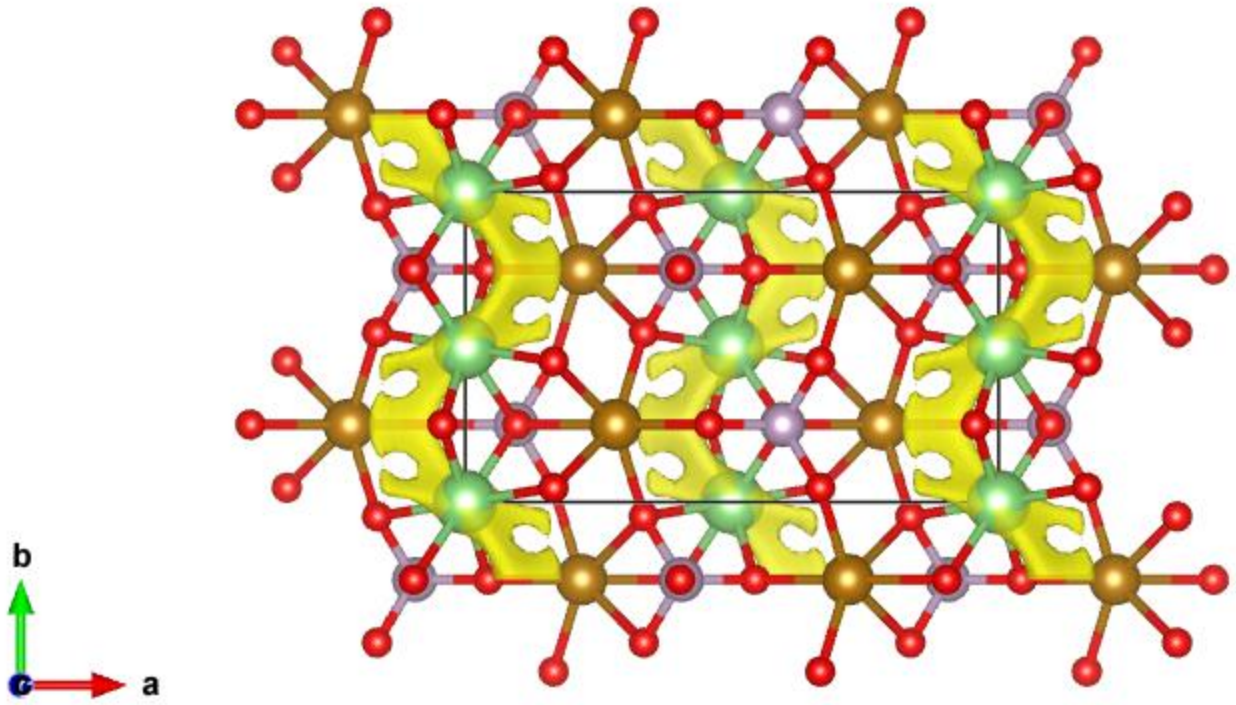
Iso-surface at energy: -3.50 eV



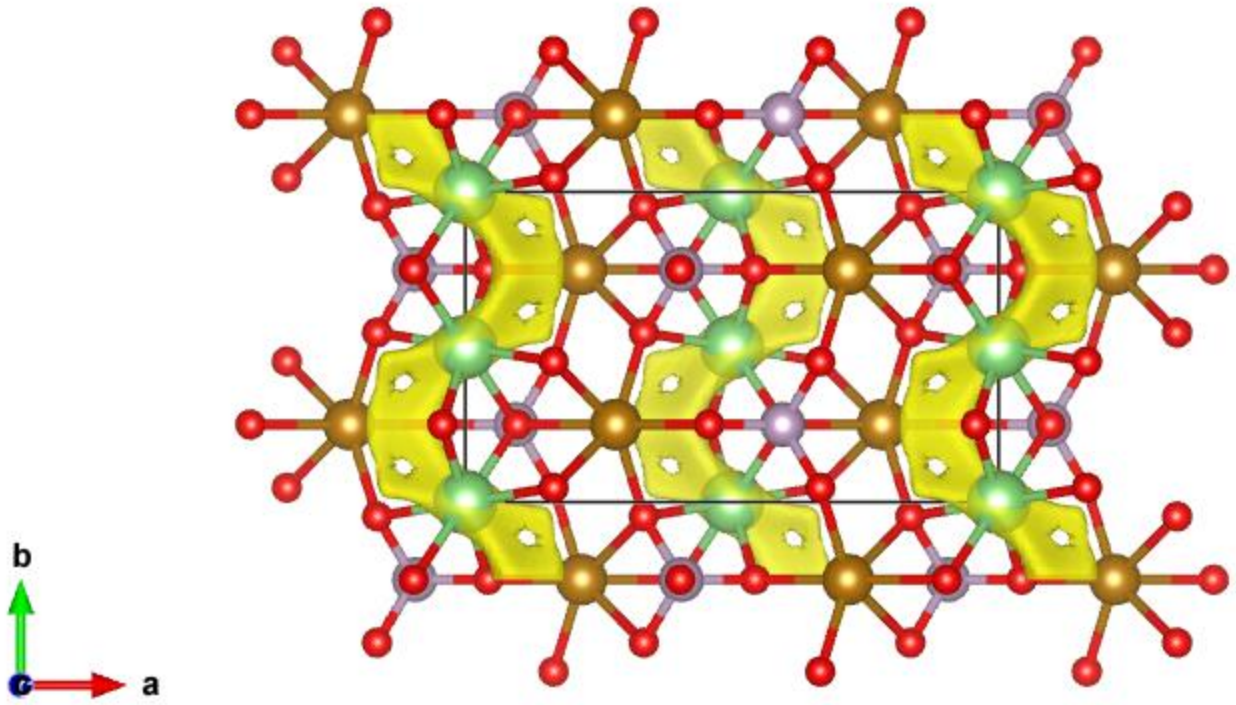
Iso-surface at energy: -3.40 eV



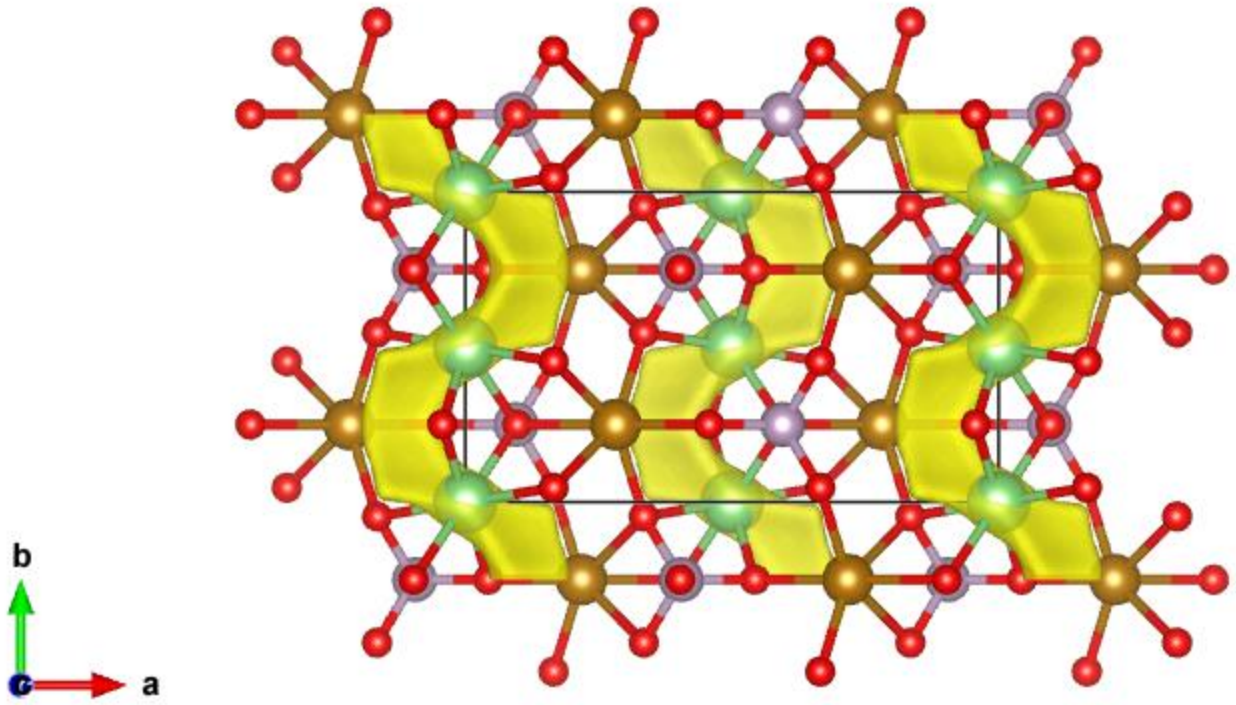
Iso-surface at energy: -3.30 eV



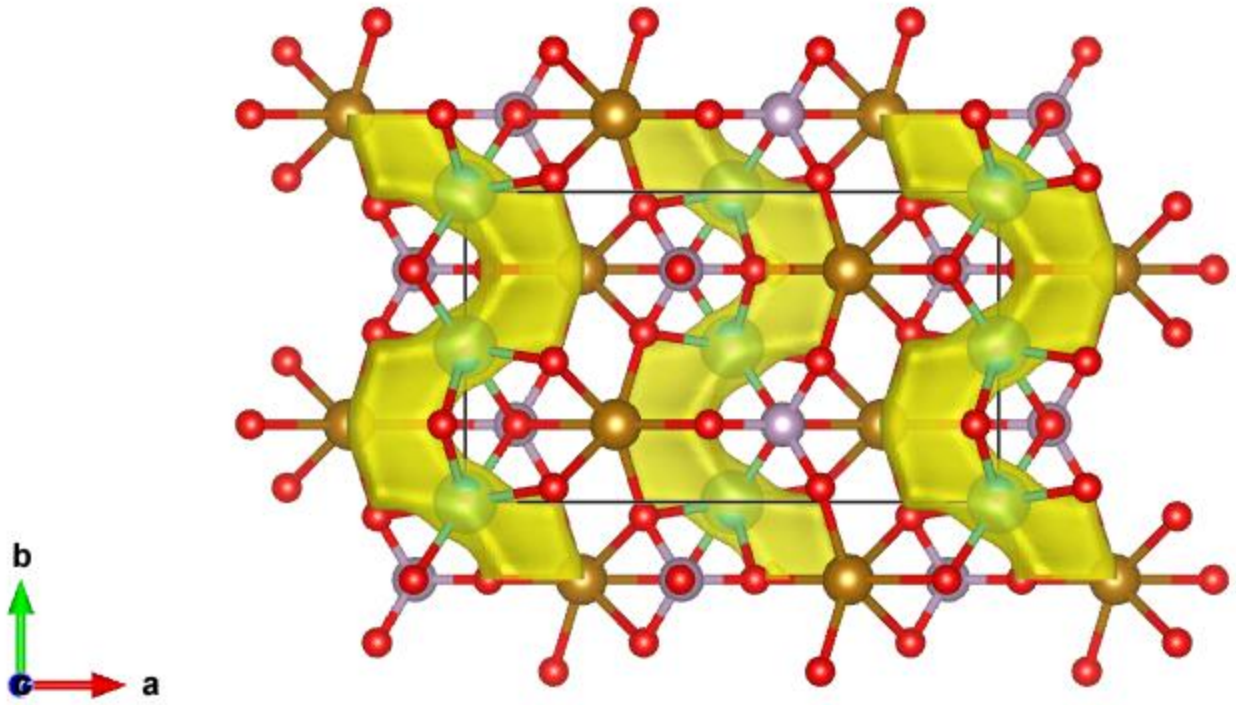
Iso-surface at energy: -3.20 eV



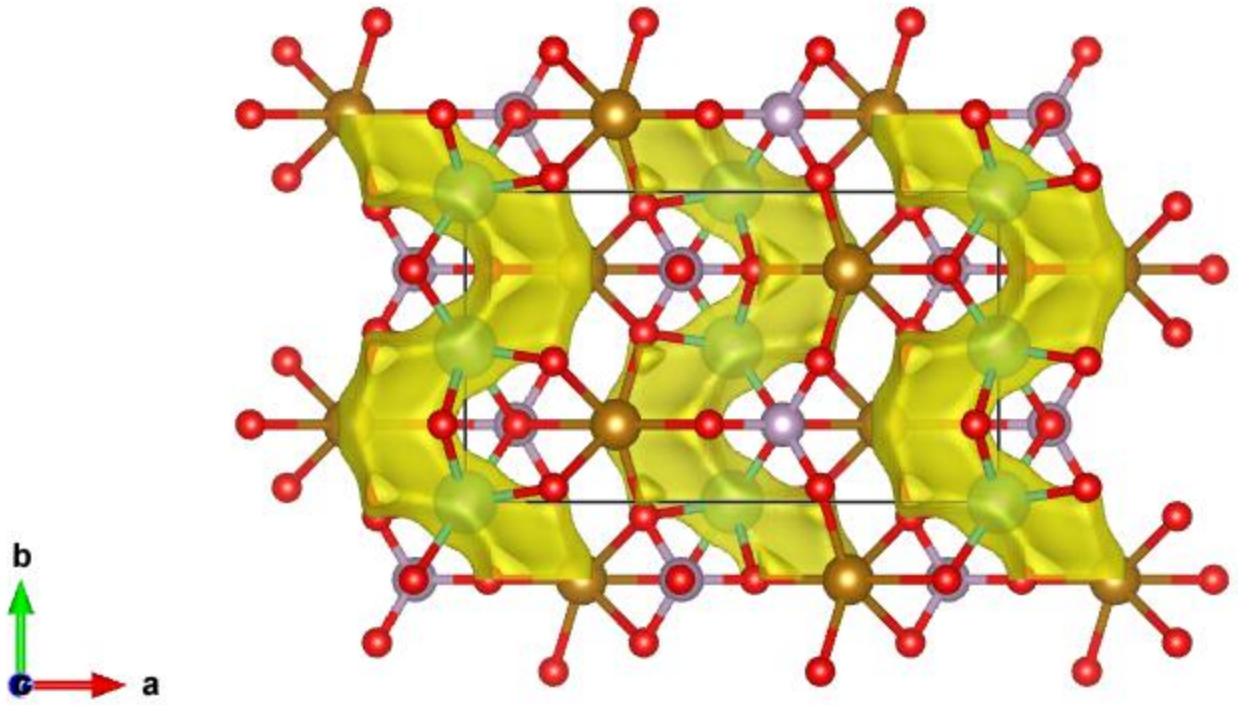
Iso-surface at energy: -3.00 eV



Iso-surface at energy: -2.00 eV



Iso-surface at energy: -1.00 eV

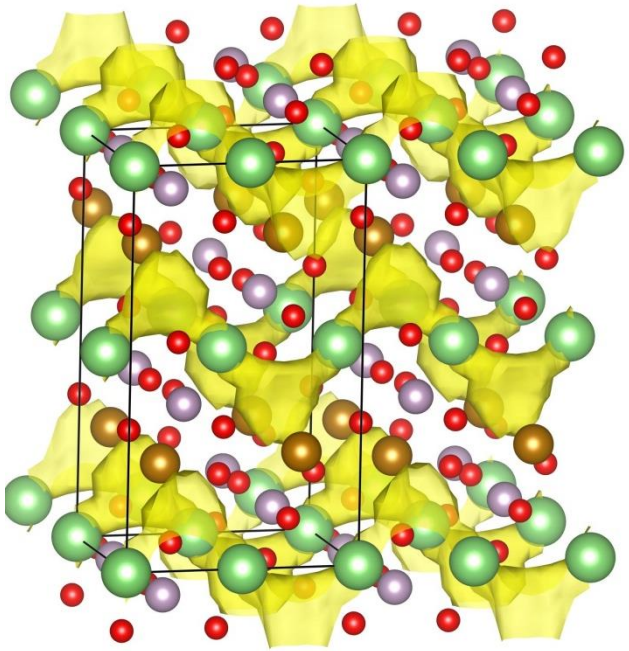


Examples of the BVEL isosurfaces

Cathodes for Li-ion batteries

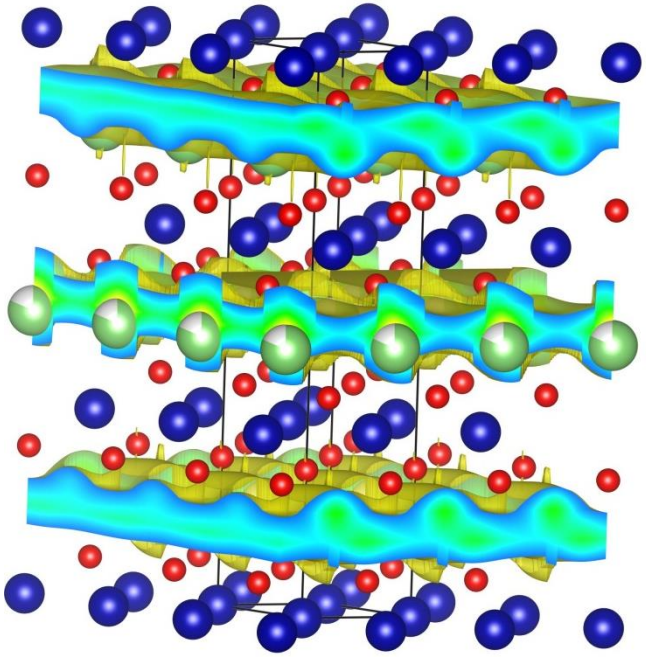
1D

Li_xFePO_4
olivine



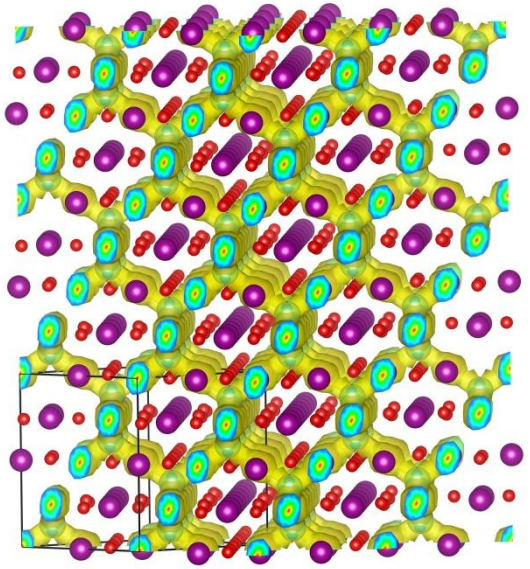
2D

Li_xCoO_2
distorted rock-salt



3D

$LiMn_2O_4$
spinel



Examples of the BVEL isosurfaces

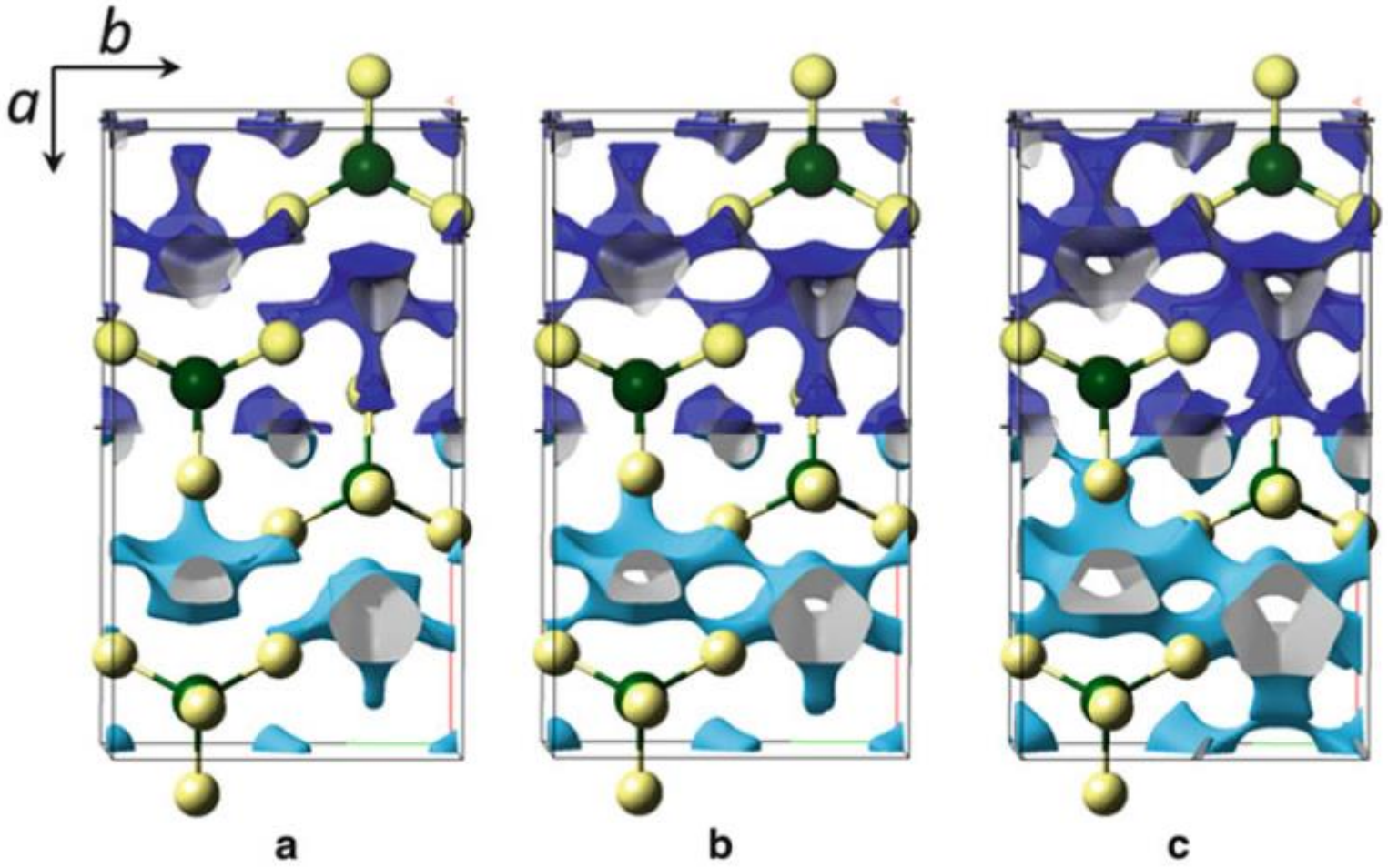


Fig. 12 Regions in the Li_4GeS_4 structure accessible to moving Li^+ ions according to BVSE energy calculations (*top half* of the unit cell) for ΔE_{BVSE} of (**a**) 0.95 eV, (**b**) 1.1 eV and (**c**) 1.35 eV and the procrystal analysis (*bottom half* of the unit cell) showing paths with electron density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

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Christoph Preiser, Jens Loesel, I. David Brown, Martin Kunz and Aniceta Skowron
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Structure and Bonding **158**, 91–128 (2014)

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