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

The Program BondStr

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NEUTRONS
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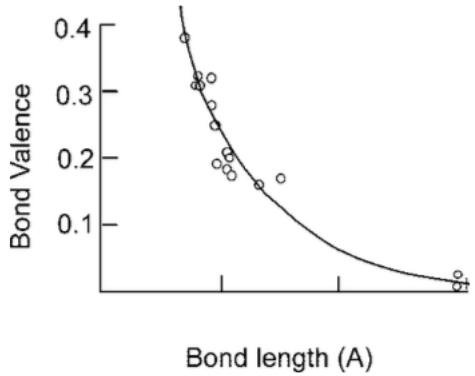
Basics of bond-valence theory

- The bond-valence method is a development of the Pauling rules
- Each bond A-X has a valence $s_{A\text{-}X}$, which depends on bond length, chemical nature of the elements and oxidation states



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

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

- **Valence sum rule**: 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.

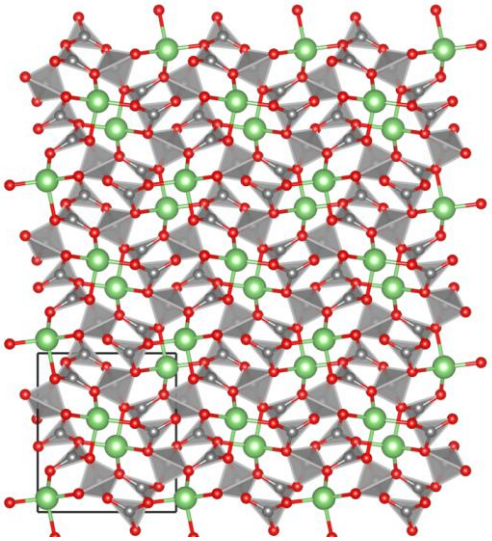
Validation of crystal structures

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

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

N_{cell} : total number of atoms in the unit cell
N_{asym} : number of atoms in the asymmetric unit
m_i : multiplicity of the site i.

An example: LiB_3O_5



Atom	Formal oxidation state	Bond valence sum	Bond valence mismatch
Li	+1	+0.856	+0.144
B	+3	+3.011	-0.011
O	-2	-1.978	-0.022

Ionic conduction and the BV method

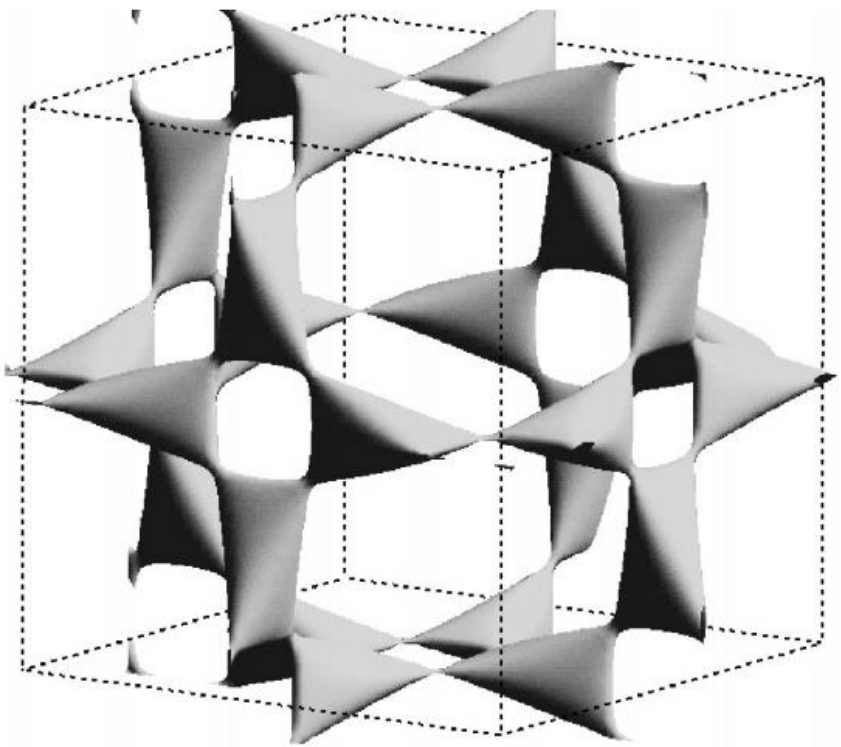
- The bond-valence method can be used for assessing the ionic conduction path from the knowledge of the crystal structure.

- 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.

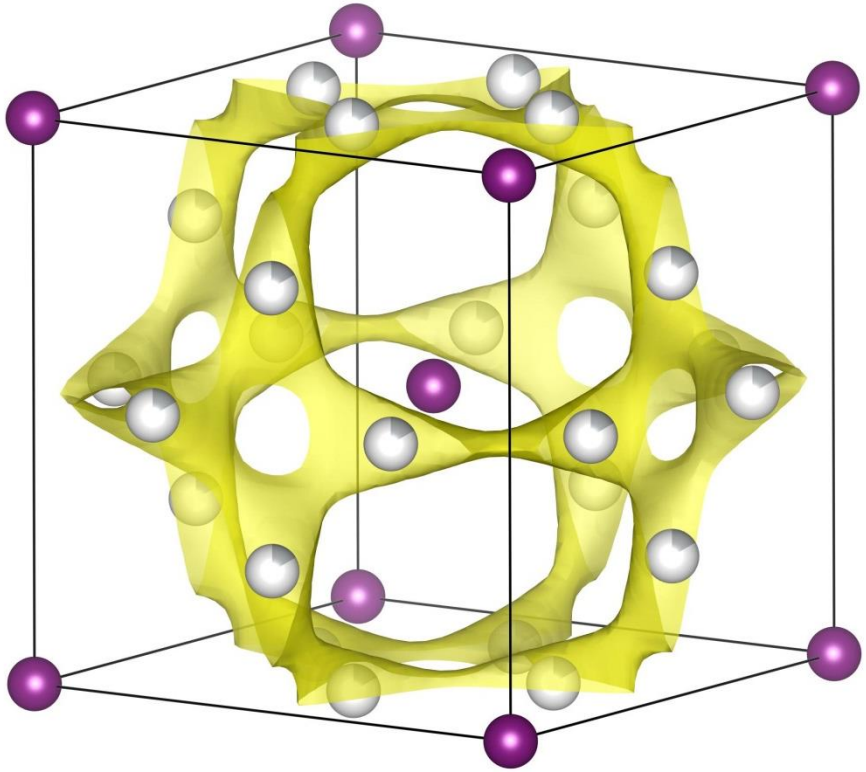
Examples of the BVS isosurfaces

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.)

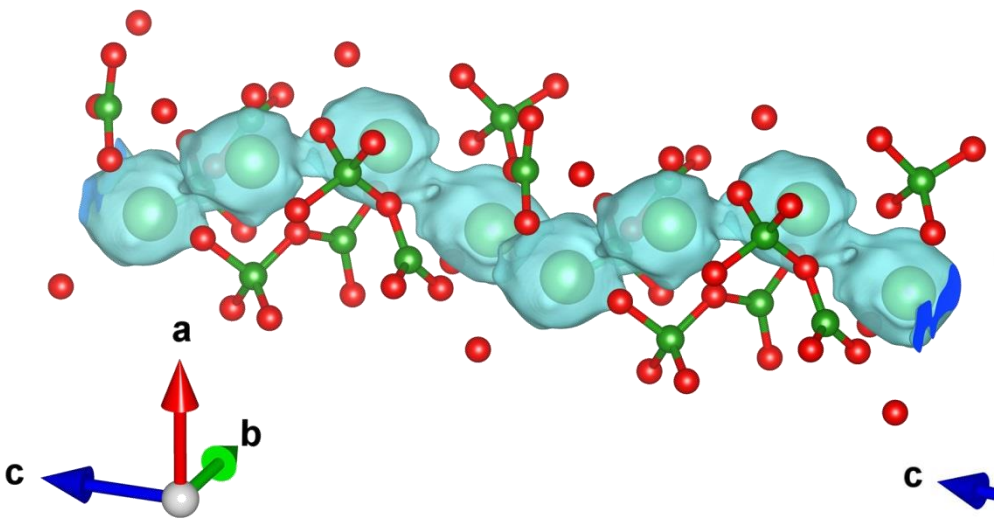
S. Adams, J. Swenson, Phys. Rev. B 63 (2000) 054201

Examples of the BVS isosurfaces

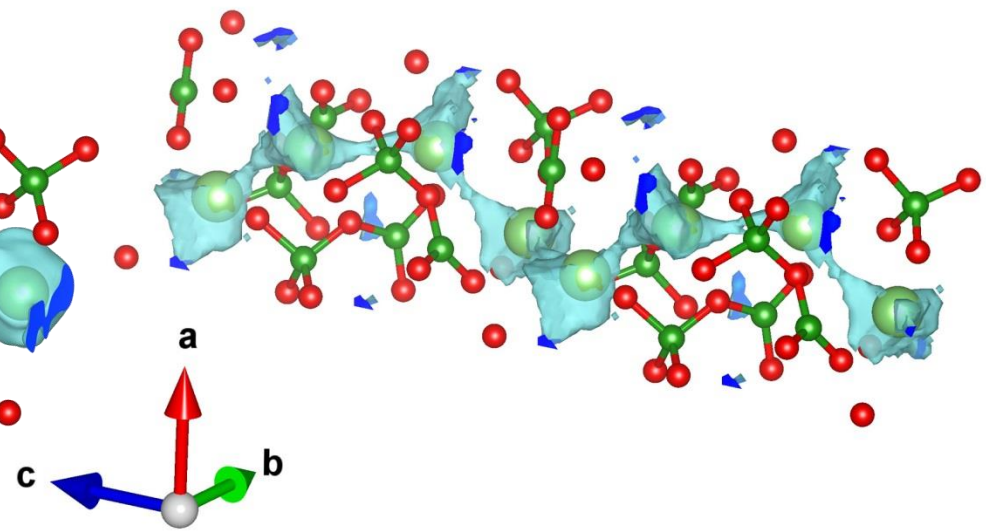
Differential bond-valence mismatch in $Li_2B_4O_7$

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

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 BV method

- **Limitation of the conventional BVS method:**
  - Only the first coordination shell is considered.
  - No energy units are available to compare between different compounds

Trick:
Use simple parameters for converting BV expression to an adequate potential (including Coulomb repulsive terms) and extend the action distance allowing to get more precise results

Ionic conduction and the BV method

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Published online: 12 February 2014

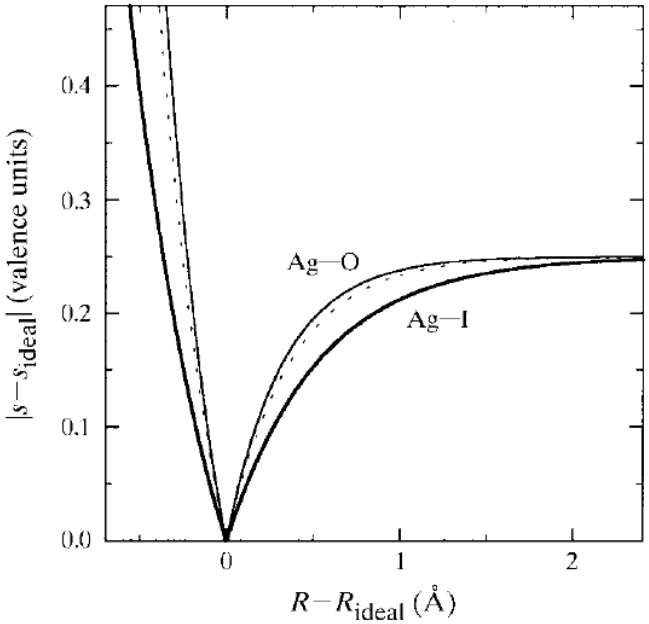
Understanding Ionic Conduction and Energy Storage Materials with Bond-Valence-Based Methods

Stefan Adams and R.Prasada Rao

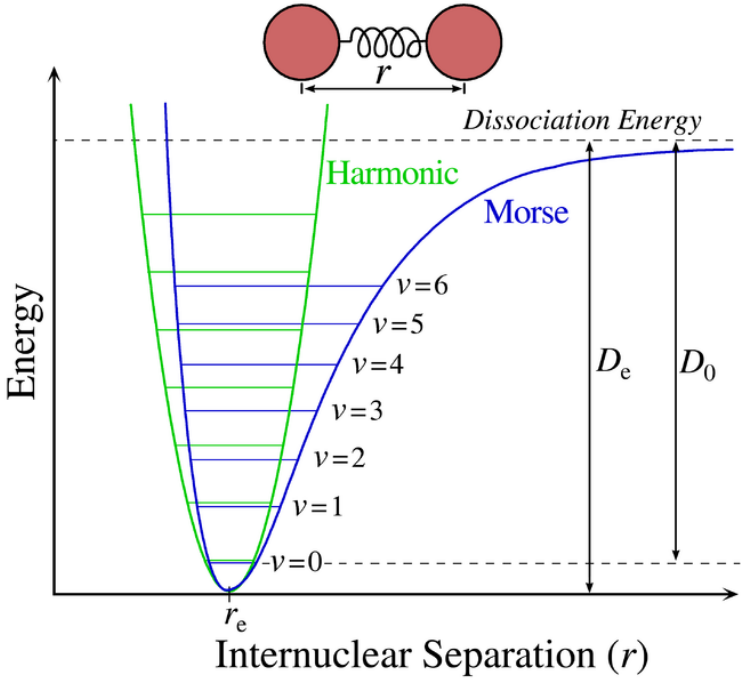
Extension of the BVS method

- 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)

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

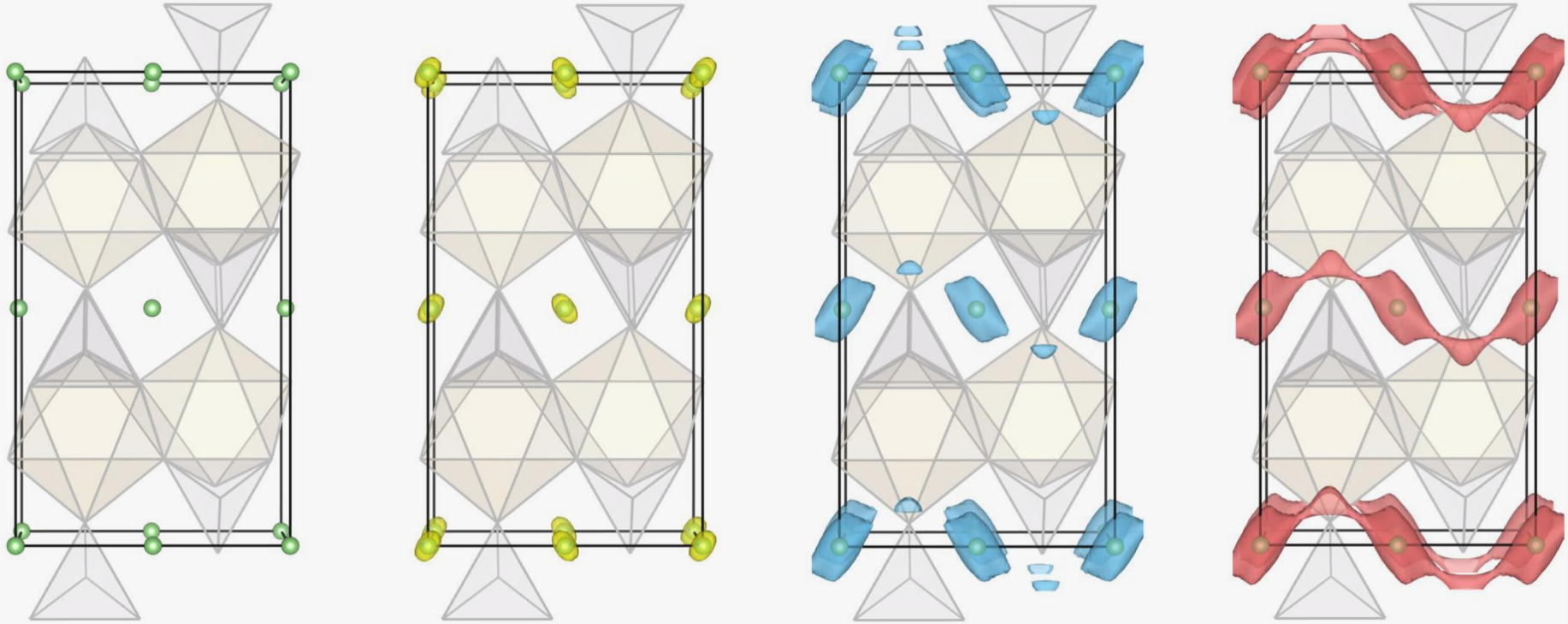
$$D_0 = \frac{kb^2}{2} = c \cdot 14.4\frac{\text{eV}}{\text{Å}}\frac{[V_{\text{id}}(\text{M}) \cdot V_{\text{id}}(\text{X})]^{1/c} b^2}{2R_{\min}\sqrt{n_{\text{M}} n_{\text{X}}}}, \qquad R_{\min} \approx R_0 \times [f_1 + f_2 \cdot |\sigma_A - \sigma_X|] - b \cdot \ln\left(\frac{V_{\text{id}}}{N_{\text{C}}}\right).$$

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

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

Extension of the BVS method

Energy isosurfaces of $LiFePO_4$



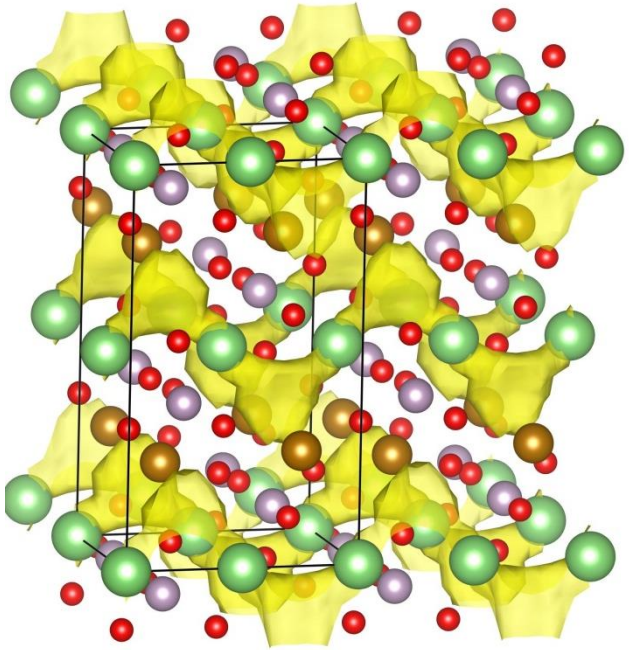
$E-E_{min} = 0.20$ eV $E-E_{min} = 0.80$ eV $E-E_{min} = 0.91$ eV

Examples of the BVEL isosurfaces

Cathodes for Li-ion batteries

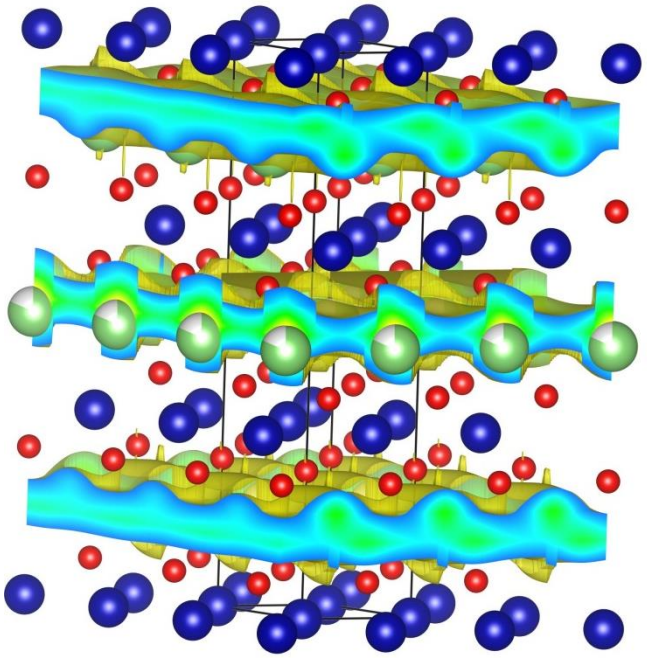
1D

Li_xFePO_4
olivine



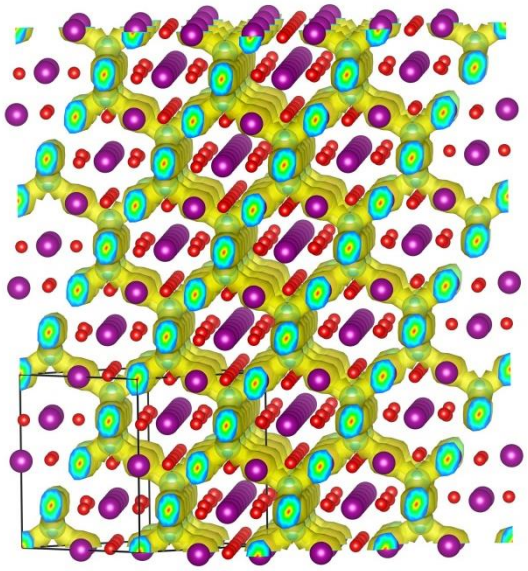
2D

Li_xCoO_2
distorted rock-salt



3D

$LiMn_2O_4$
spinel



Examples of the BVEL isosurfaces

BVEL

DFT

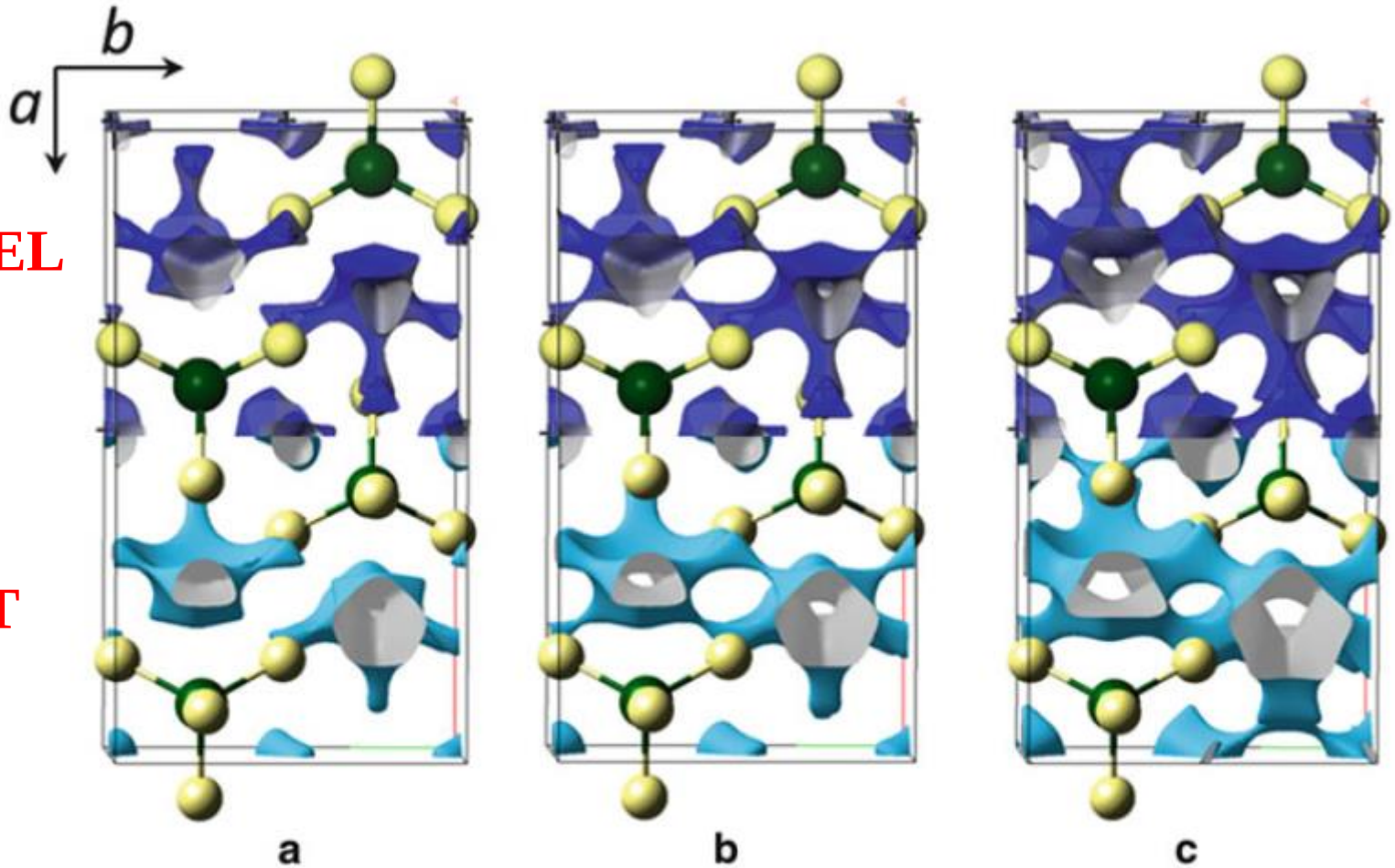


Fig. 12 Regions in the Li_4GeS_4 structure accessible to moving Li^+ ions according to BVSE energy calculations (*top half* of the unit cell) for ΔE_{BVSE} of (**a**) 0.95 eV, (**b**) 1.1 eV and (**c**) 1.35 eV and the procrystal analysis (*bottom half* of the unit cell) showing paths with electron density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

Computer programs

computer programs

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

Matthew Sale* and Maxim Avdeev*

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

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

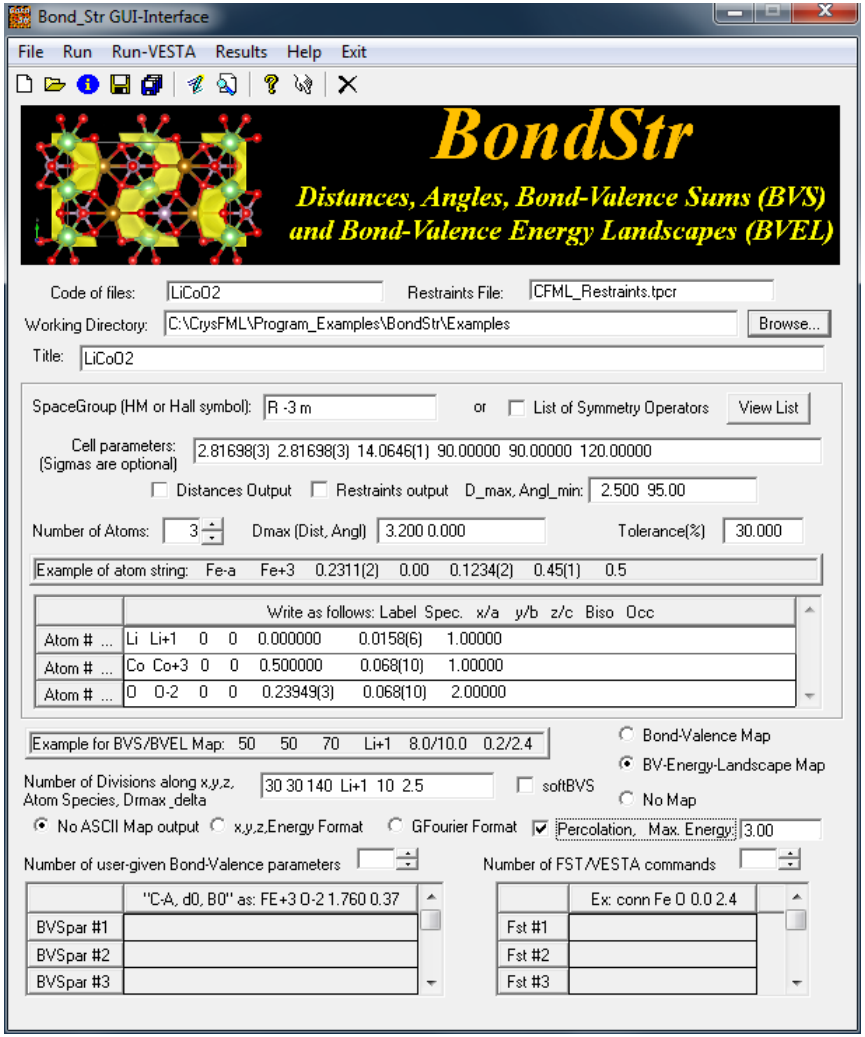
The program needs the use of Materials Studio

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

The BondStr program

Features:

- BV and BVEL maps
- Map visualization with VESTA
- Automatic assignation of formal charges
- Automatic detection of percolation energy
- High-throughput calculations
- Distributed within the FullProf suite



The BondStr program: the output

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

File Edit Actions Options Window Help

```
====>
    ---------------------------------------------------
       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

The BondStr program: the output

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

File Edit Actions Options Window Help

```
====>

 => 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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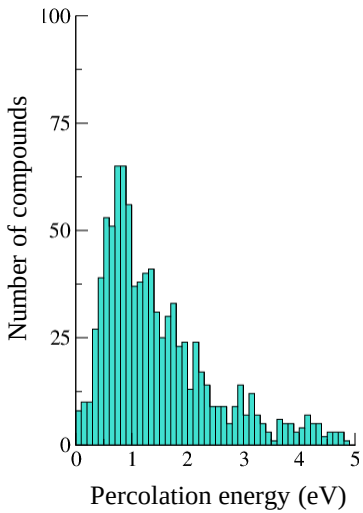
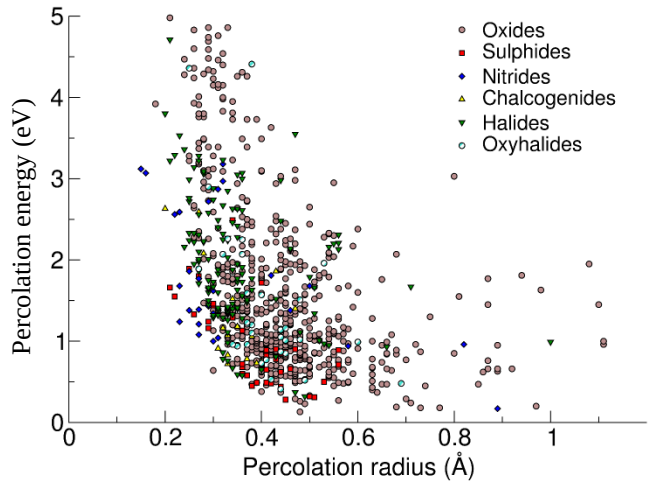
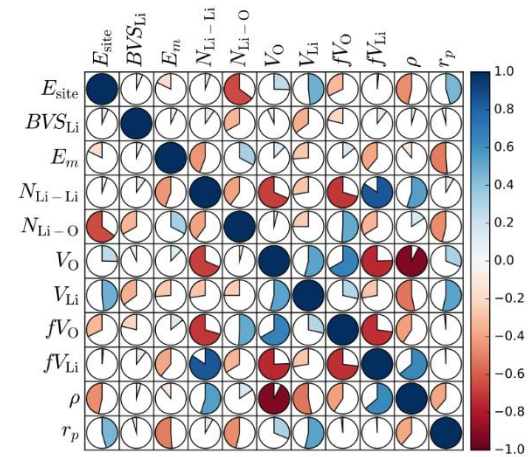
Screening the ICSD with BondStr

- We have used BondStr to investigate the crystal structure – ion conductivity relation in Li and Na compounds

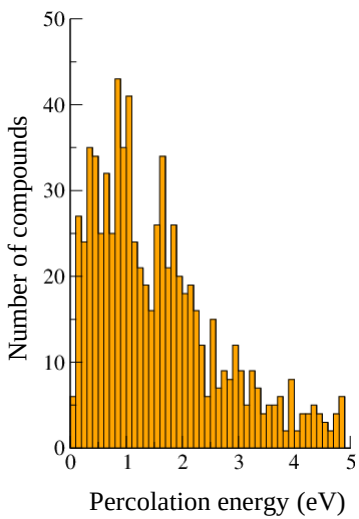
Li

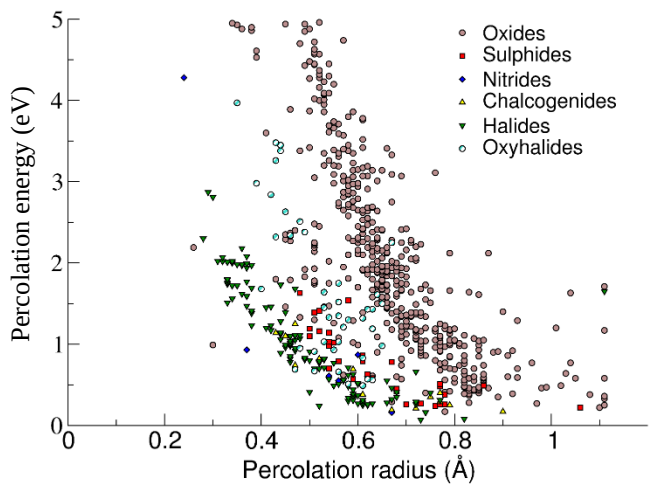


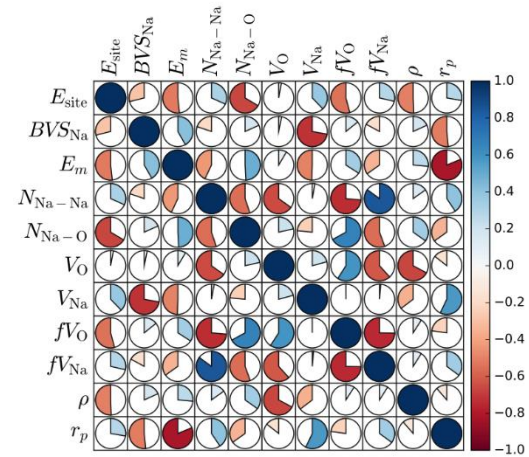




Na







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