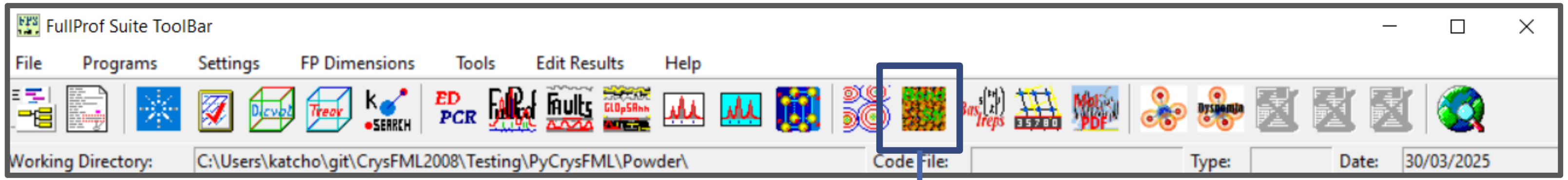
The program BondStr: an implementation of bond-valence theory

The Graphical User Interface of BondStr

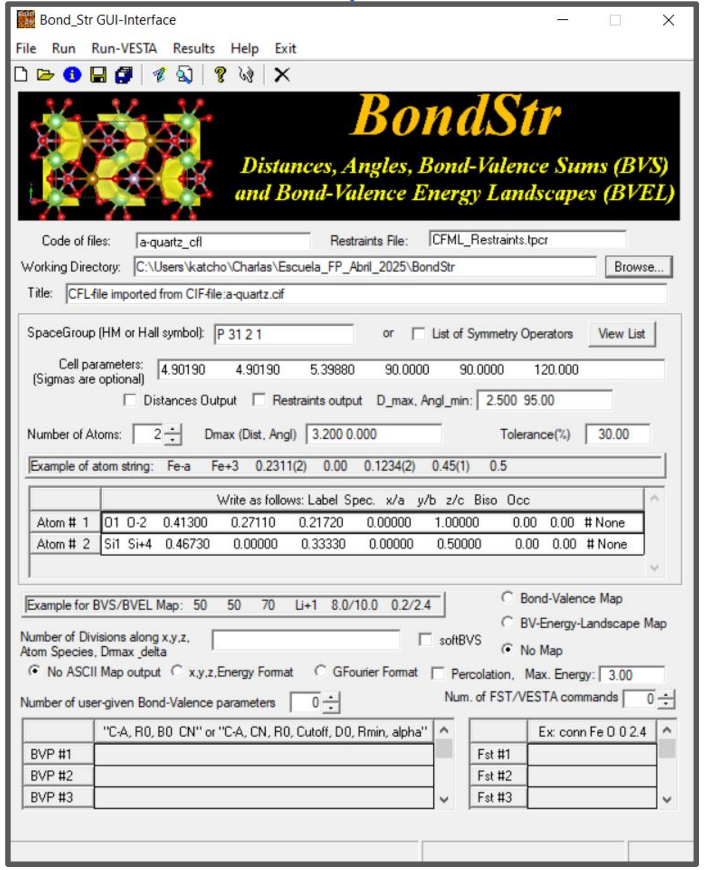


Working Directory: C:\Users\katcho\git\CrysFML2008\Testing\PyCrysFML\Powder\

Code File:

Type:

Date: 30/03/2025



Code of files: a-quartz_cfl

Restraints File: CFML_Restraints.tpcr

Working Directory: C:\Users\katcho\Charlas\Escuela_FP_Abril_2025\BondStr

Title: CFL-file imported from CIF-file:a-quartz.cif

SpaceGroup (HM or Hall symbol): P 31 2 1 or ☐ List of Symmetry Operators

Cell parameters: (Sigmas are optional) 4.90190 4.90190 5.39880 90.0000 90.0000 120.000

☐ Distances Output ☐ Restraints output D_max, Angl_min: 2.500 95.00

Number of Atoms: 2

Dmax (Dist, Angl) 3.200 0.000

Tolerance(%) 30.00

Example of atom string: Fe-a Fe+3 0.2311(2) 0.00 0.1234(2) 0.45(1) 0.5

	Write as follows: Label Spec. x/a y/b z/c Biso Occ
Atom # 1	O1 O-2 0.41300 0.27110 0.21720 0.00000 1.00000 0.00 0.00 # None
Atom # 2	Si1 Si+4 0.46730 0.00000 0.33330 0.00000 0.50000 0.00 0.00 # None

Example for BVS/BVEL Map: 50 50 70 Li+1 8.0/10.0 0.2/2.4

○ Bond-Valence Map

○ BV-Energy-Landscape Map

● No Map

Number of Divisions along x,y,z, Atom Species, Drmax _delta

☐ softBVS

● No ASCII Map output ○ x,y,z,Energy Format ○ GFourier Format ☐ Percolation, Max. Energy: 3.00

Number of user-given Bond-Valence parameters 0

Num. of FST/VESTA commands 0

	"C-A, R0, B0 CN" or "C-A, CN, R0, Cutoff, D0, Rmin, alpha"
BVP #1	
BVP #2	
BVP #3	

	Ex: conn Fe O 0 2.4
Fst #1	
Fst #2	
Fst #3	

Pauling rules

- **Pauling rules** are a series of structural principles for ionic compounds.

First rule: Coordination polyhedral
A coordination polyhedron of anions is formed around every cation. The cation-anion distances are determined by the sum of the ionic radii, and the coordination number of the cation by the radius ratio.

Second rule: The electrostatic valence rule
In a stable ionic structure the valence (ionic charge) of each anion with changed sign is exactly or nearly equal to the sum of the electrostatic bond strengths to it from adjacent cations. The electrostatic bond strength is defined as the ratio of the charge on a cation to its coordination number.

Bond strengths: calculation

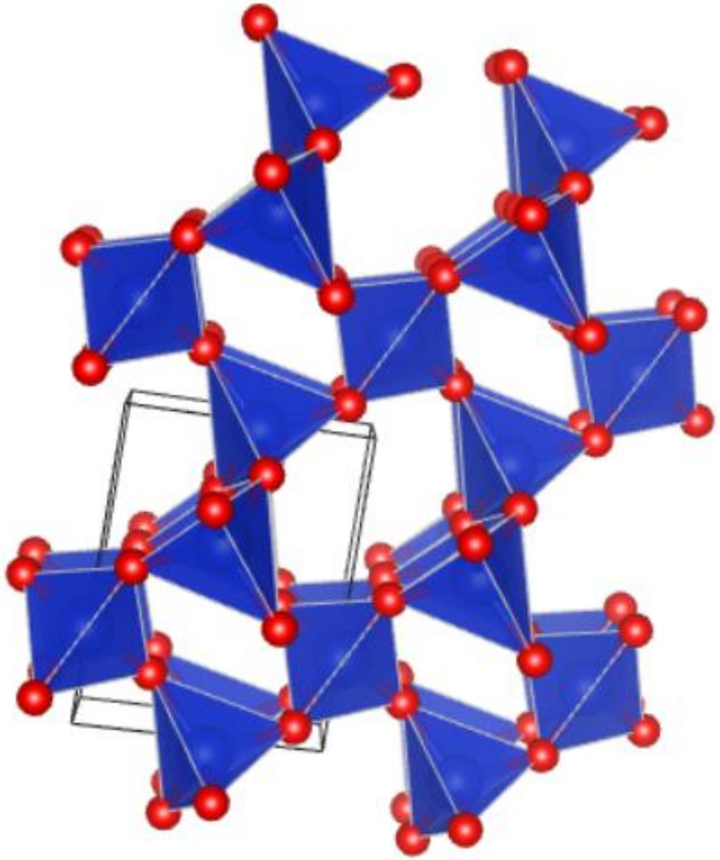
s_i : bond strength for cation i
q_{i+}: atomic charge (valence) of cation i
n_{i+}: coordination number of cation i
q_{j-}: atomic charge (valence) of anion j
n_{j-}: coordination number of anion j

$$s_i = \frac{q_{i+}}{n_{i+}}$$

$$q_{j-} = \sum_{i=1}^{n_{j-}} s_i$$

Bond strengths: an example

α-SiO_2 (quartz)



→

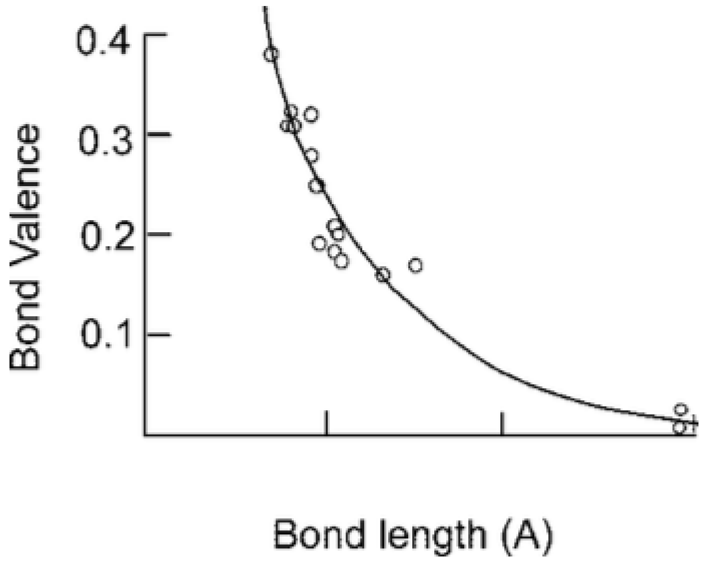
$q_{Si} = +4; n_{Si} = 4; n_O = 2$

$$s_{Si} = \frac{q_{Si}}{n_{Si}} = \frac{4}{4} = 1$$

$$q_O = -\sum_{i=1}^{2} s_i = -1 - 1 = -2$$

Basics of bond-valence theory

- The bond-valence theory is a development of the **Pauling rules**.
- Each bond A-X has a bond strength $s_{A\text{-}X}$, 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 $A\text{-}X$ and $R_{A\text{-}X}$ is the bond length

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

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

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

↓

Atomic valences can be computed from bond distances

Validation of crystal structures

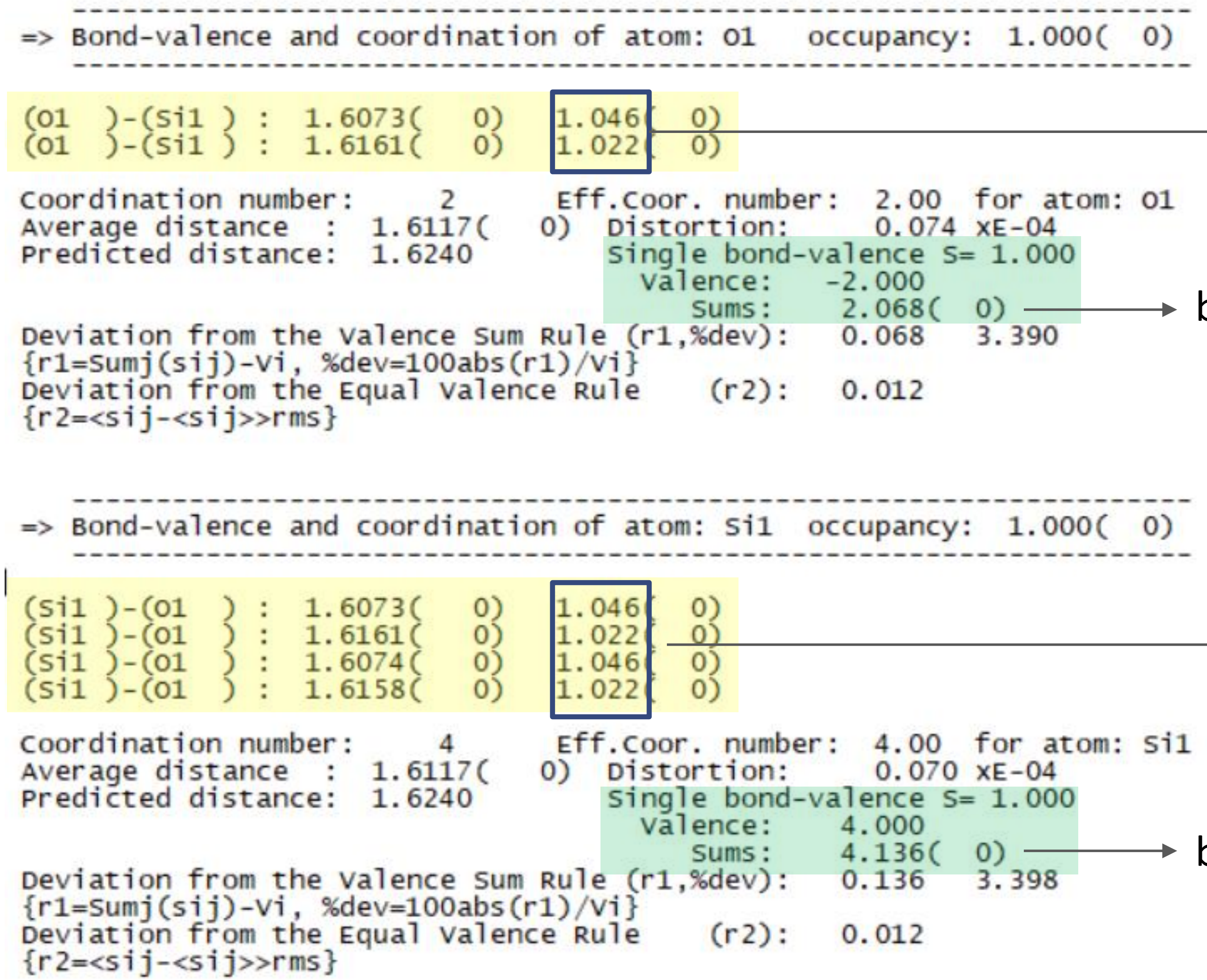
- The bond valence approach is frequently used to validate newly determined crystal structures by the calculation of the **Global Instability Index (GII)**

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

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*.

- In stable, well determined structures, theGII is usually less than **0.1** valence units. Values between **0.1**and **0.2** indicate a strained structure, whereas higher values are unusual and can point to an incorrect structure determination.

An example: α-SiO_2



```
      ------------------------------------------------------------------
   => Bond-valence and coordination of atom: O1    occupancy:  1.000(  0)
      ------------------------------------------------------------------

   (O1  )-(Si1 ) :  1.6073(   0)  1.046(  0)
   (O1  )-(Si1 ) :  1.6161(   0)  1.022(  0)

   Coordination number:     2      Eff.Coor. number:  2.00  for atom: O1
   Average distance  :  1.6117(   0)  Distortion:      0.074 xE-04
   Predicted distance:  1.6240        Single bond-valence S= 1.000
                                        Valence:    -2.000
                                           Sums:     2.068(  0)
   Deviation from the Valence Sum Rule (r1,%dev):    0.068   3.390
   {r1=Sumj(sij)-Vi, %dev=100abs(r1)/Vi}
   Deviation from the Equal Valence Rule     (r2):    0.012
   {r2=<sij-<sij>>rms}


      ------------------------------------------------------------------
   => Bond-valence and coordination of atom: Si1   occupancy:  1.000(  0)
      ------------------------------------------------------------------

   (Si1 )-(O1   ) :  1.6073(   0)  1.046(  0)
   (Si1 )-(O1   ) :  1.6161(   0)  1.022(  0)
   (Si1 )-(O1   ) :  1.6074(   0)  1.046(  0)
   (Si1 )-(O1   ) :  1.6158(   0)  1.022(  0)

   Coordination number:     4      Eff.Coor. number:  4.00  for atom: Si1
   Average distance  :  1.6117(   0)  Distortion:      0.070 xE-04
   Predicted distance:  1.6240        Single bond-valence S= 1.000
                                        Valence:     4.000
                                           Sums:     4.136(  0)
   Deviation from the Valence Sum Rule (r1,%dev):    0.136   3.398
   {r1=Sumj(sij)-Vi, %dev=100abs(r1)/Vi}
   Deviation from the Equal Valence Rule     (r2):    0.012
   {r2=<sij-<sij>>rms}
```

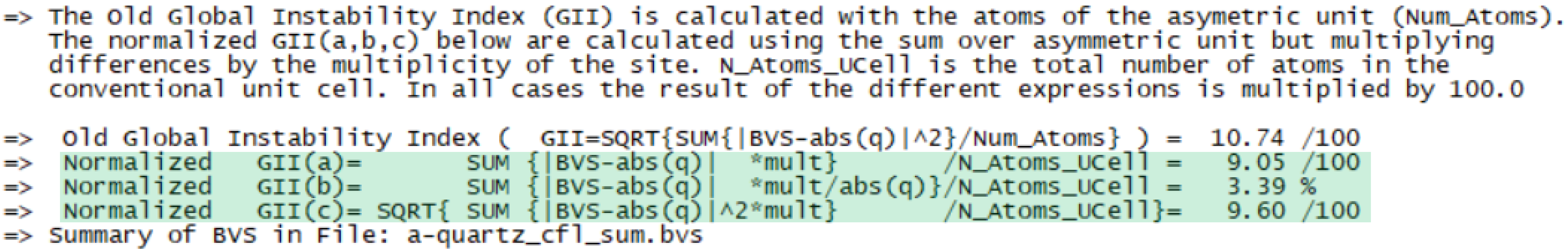
individual bond strengths

bond-valence sum

individual bond strengths

bond-valence sum

An example: α-SiO_2



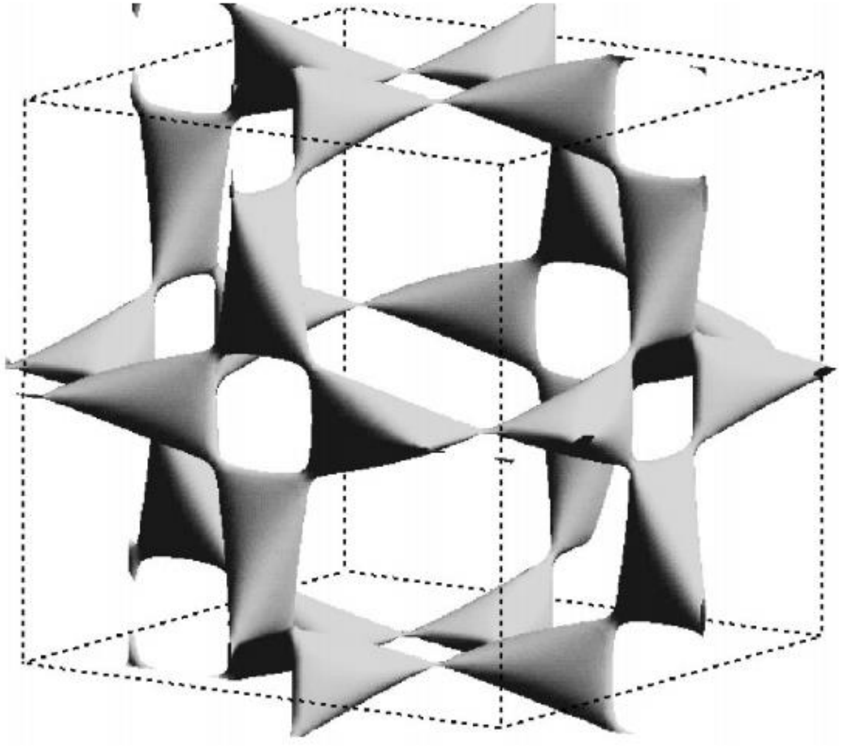
```
=> The Old Global Instability Index (GII) is calculated with the atoms of the asymetric unit (Num_Atoms).
   The normalized GII(a,b,c) below are calculated using the sum over asymmetric unit but multiplying
   differences by the multiplicity of the site. N_Atoms_UCell is the total number of atoms in the
   conventional unit cell. In all cases the result of the different expressions is multiplied by 100.0

=>  Old Global Instability Index (  GII=SQRT{SUM{|BVS-abs(q)|^2}/Num_Atoms} ) =  10.74 /100
=>  Normalized   GII(a)=       SUM {|BVS-abs(q)|  *mult}       /N_Atoms_UCell =   9.05 /100
=>  Normalized   GII(b)=       SUM {|BVS-abs(q)|  *mult/abs(q)}/N_Atoms_UCell =   3.39 %
=>  Normalized   GII(c)= SQRT{ SUM {|BVS-abs(q)|^2*mult}       /N_Atoms_UCell}=   9.60 /100
=> Summary of BVS in File: a-quartz_cfl_sum.bvs
```

Ionic conductivty

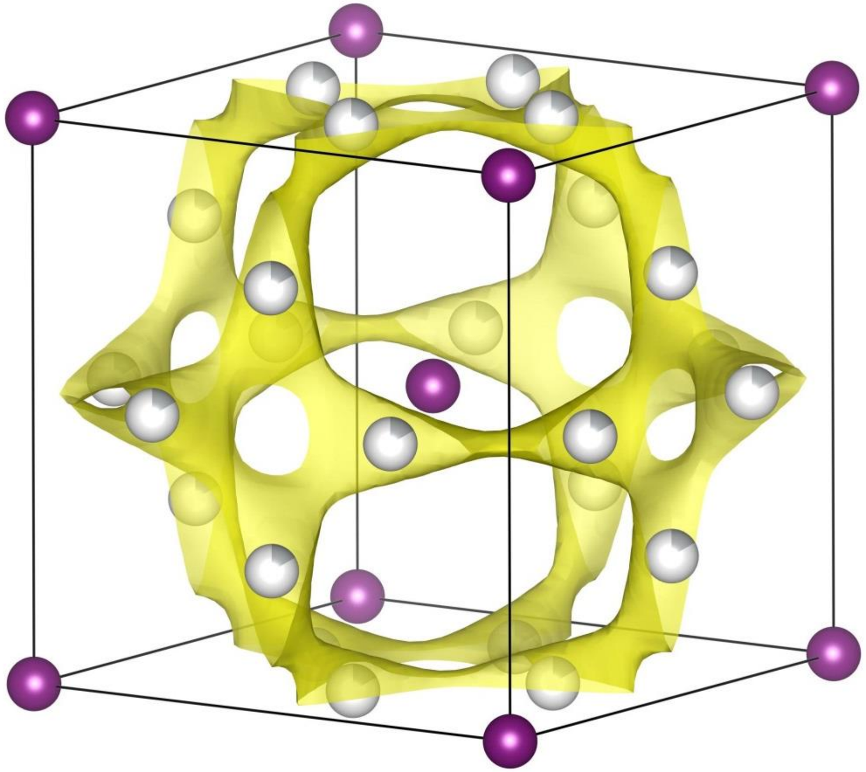
- The bond-valence method can be used for assessing the ionic conduction path from the knowledge of the crystal structure.

- 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.

Bond-valence mismatch



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

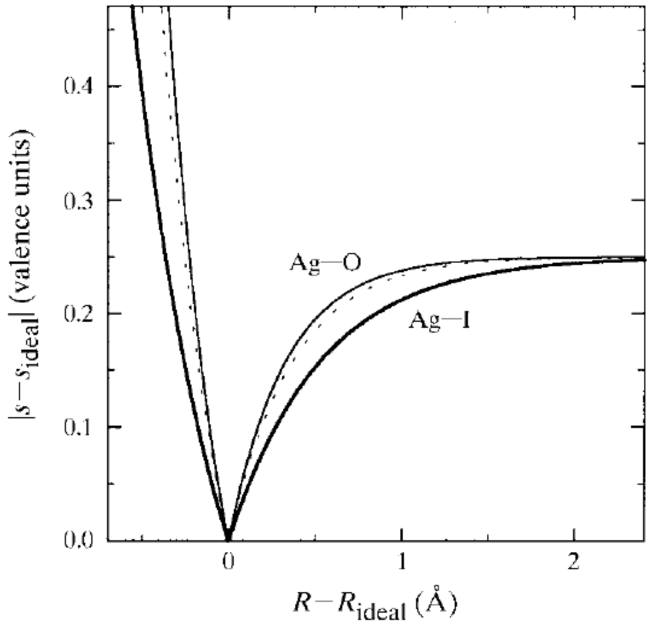


Bond valence isosurface
for α-AgI (ΔV=0.083 val. un.)

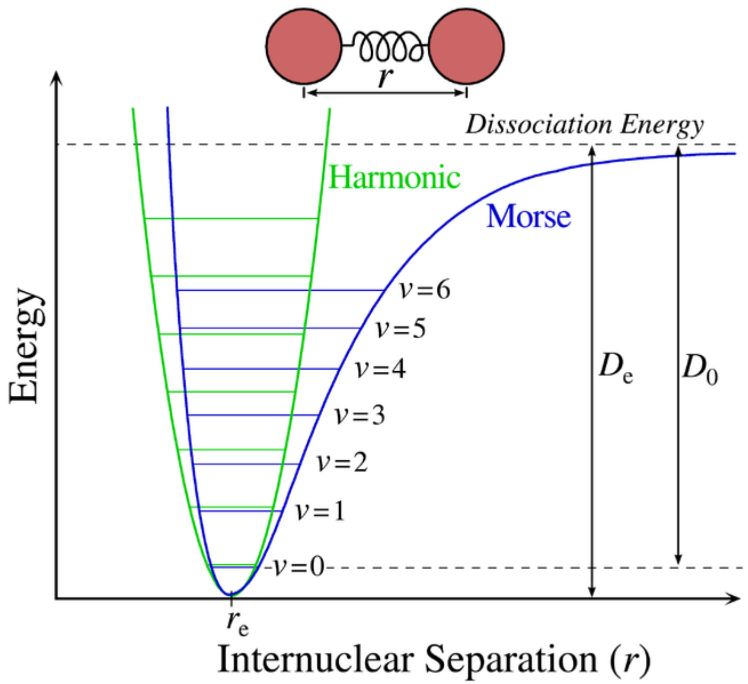
S. Adams, J. Swenson, Phys. Rev. B 63 (2000) 054201

Bond-valence energy landscape

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



Typical Morse potential



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

Bond-valence energy landscape

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

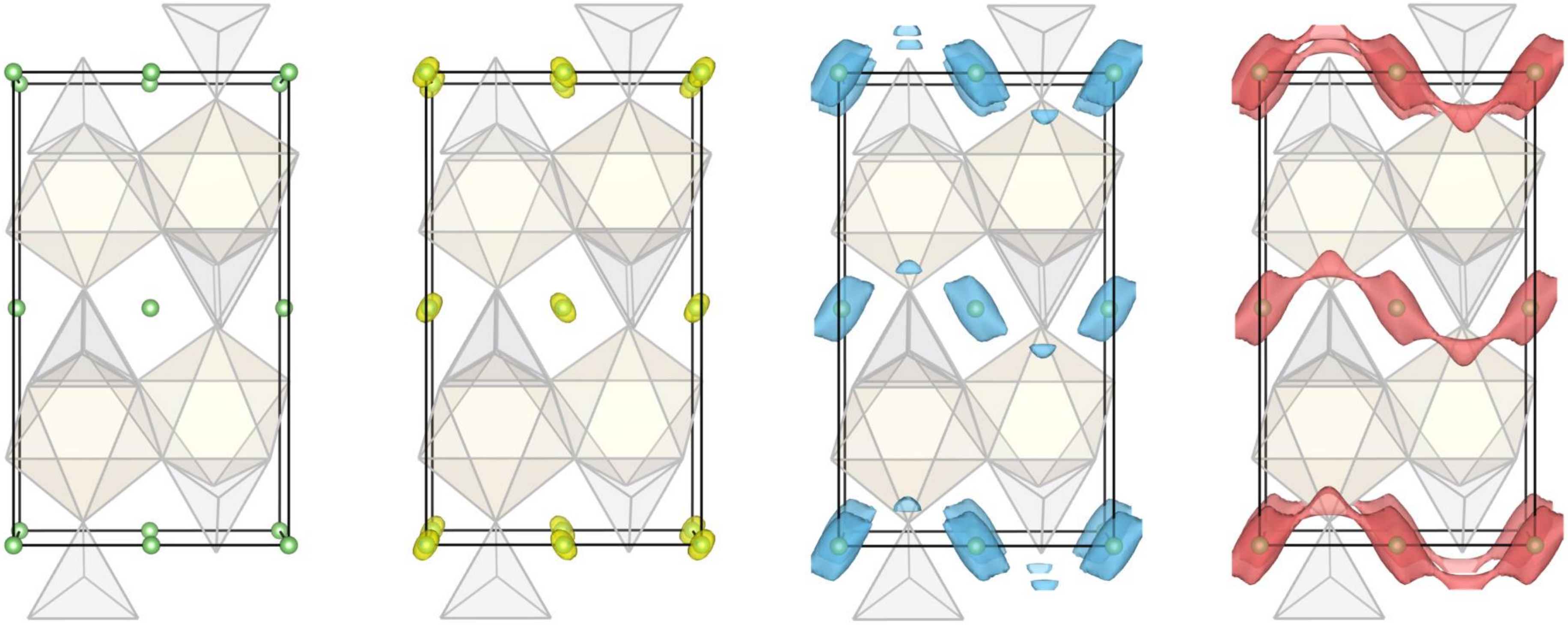
$$E = D_0\left\{\left(\exp[\alpha(R_{\mathrm{min}} - R)] - 1\right)^2 - 1\right\}$$
$$= D_0\left\{\left(\frac{\exp\left[\frac{R_0 - R}{b}\right] - s_{\mathrm{min}}}{s_{\mathrm{min}}}\right)^2 - 1\right\}$$

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

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

An example: $LiFePO_4$

Energy isosurfaces of $LiFePO_4$

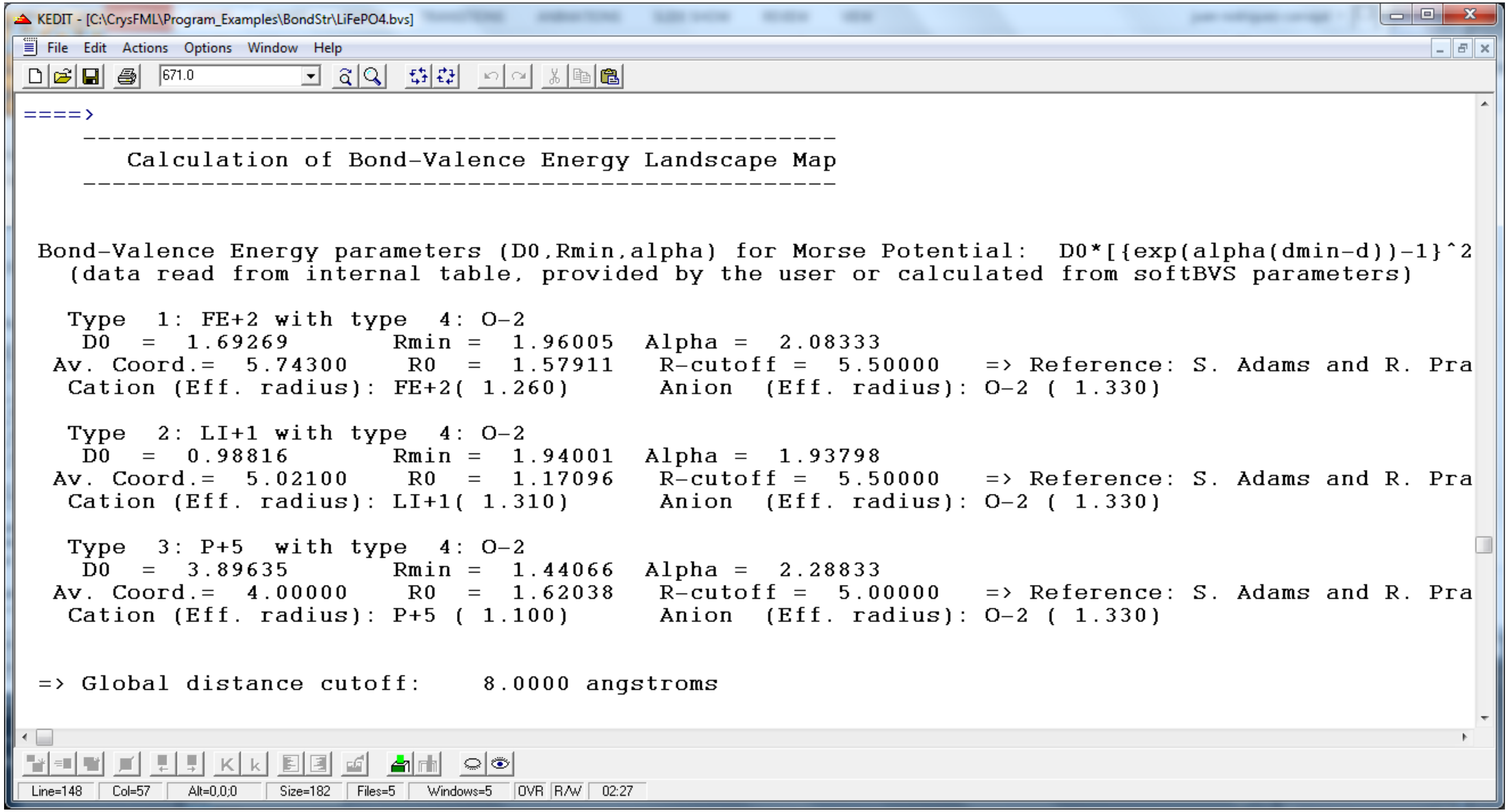


$E-E_{min} = 0.20$ eV

$E-E_{min} = 0.80$ eV

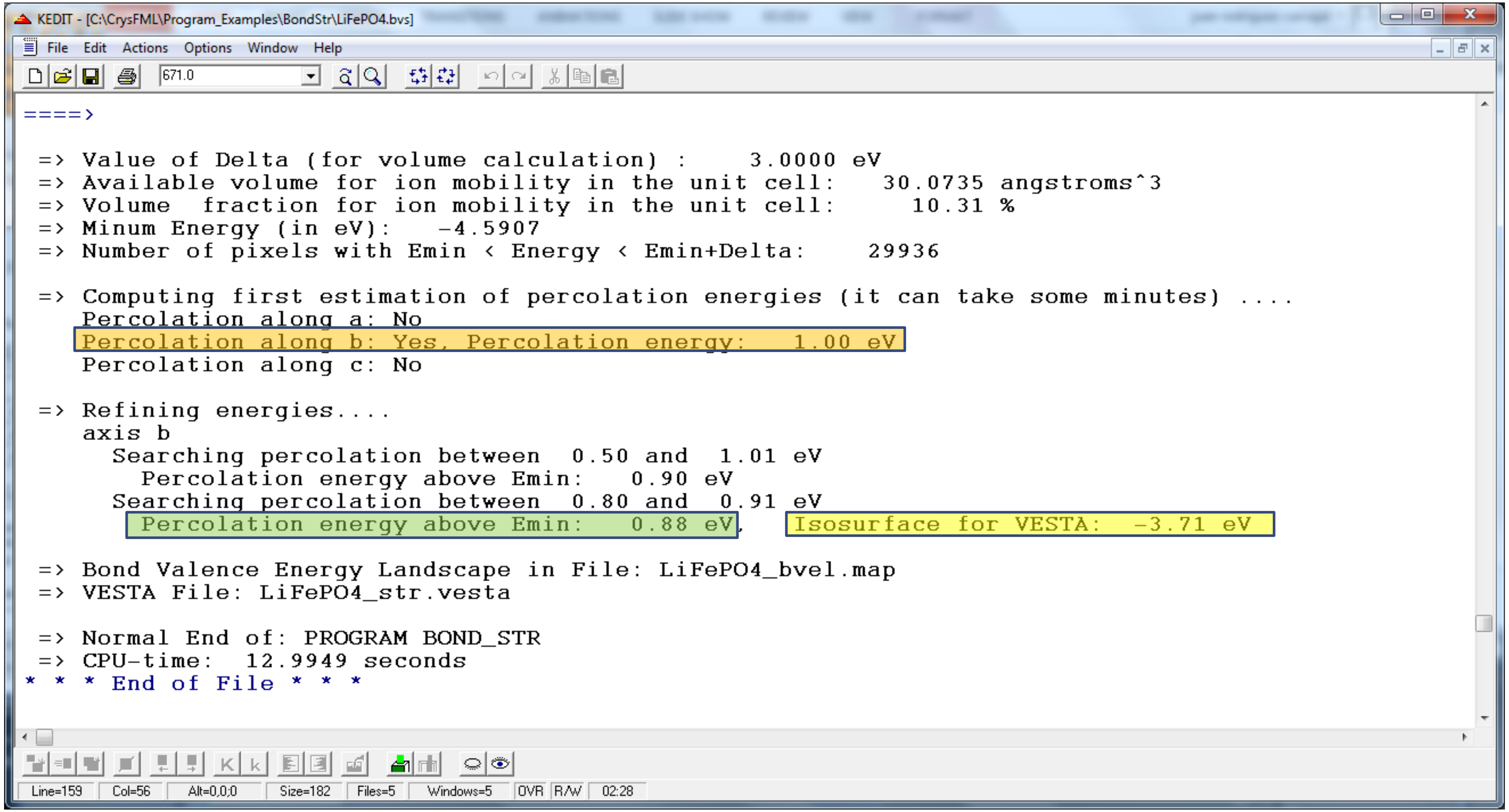
$E-E_{min} = 0.91$ eV

An example: $LiFePO_4$



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

An example: $LiFePO_4$



```
====>

  => 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 * * *
```

BVEL vs DFT

BVEL

DFT

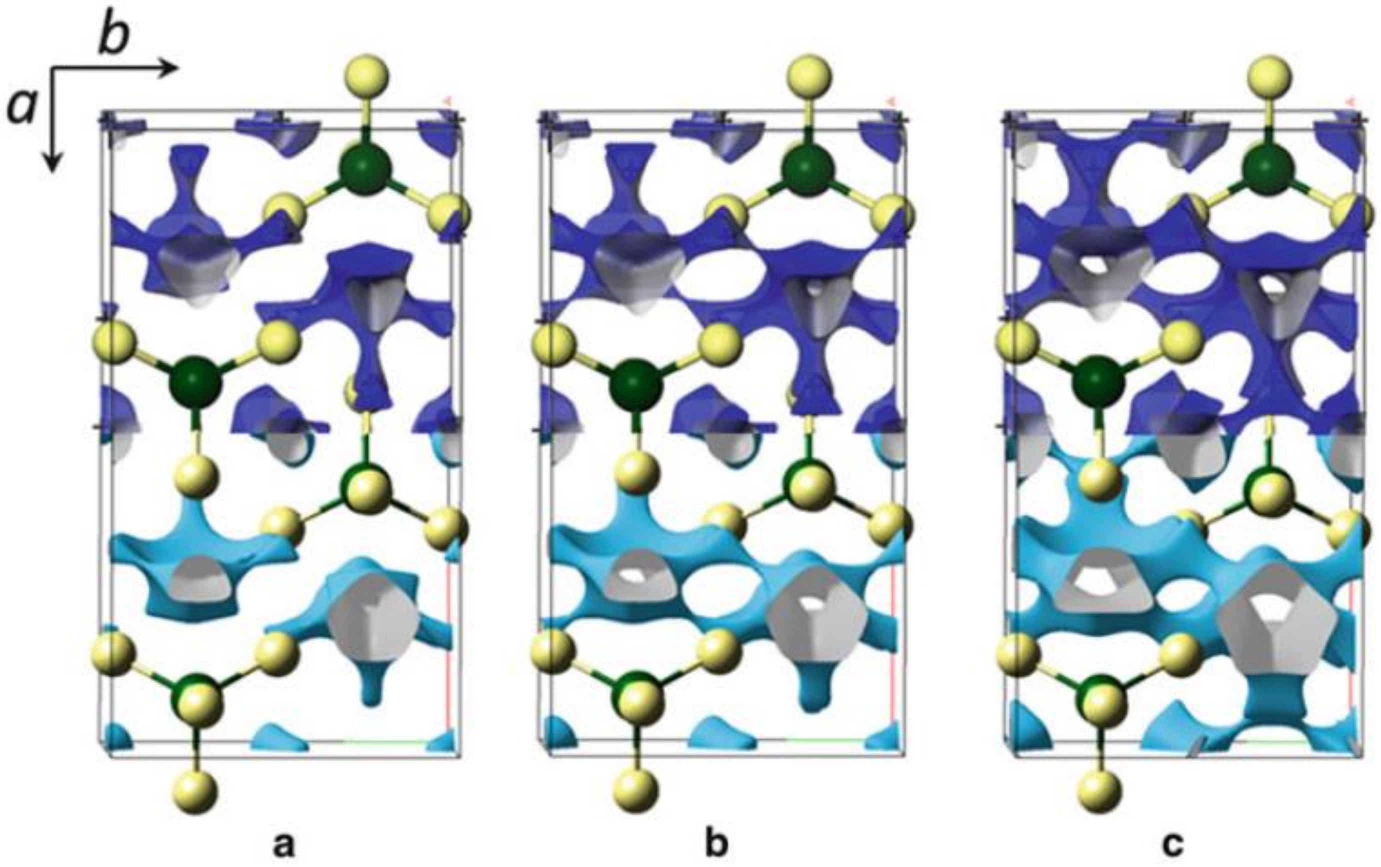


Fig. 12 Regions in the Li_4GeS_4 structure accessible to moving Li^+ ions according to BVSE energy calculations (*top half* of the unit cell) for ΔE_{BVSE} of (**a**) 0.95 eV, (**b**) 1.1 eV and (**c**) 1.35 eV and the procrystal analysis (*bottom half* of the unit cell) showing paths with electron density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

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 …

- The BVEL Model is restricted to compounds close to ionic character; e.g. it does not, in general, apply to metals or organic compounds