Prof. Elena Levi

24 year of work in the lab of prof. D. Aurbach (from 1995)

1981 - PhD in Geochemistry and Crystallography, Moskow State University

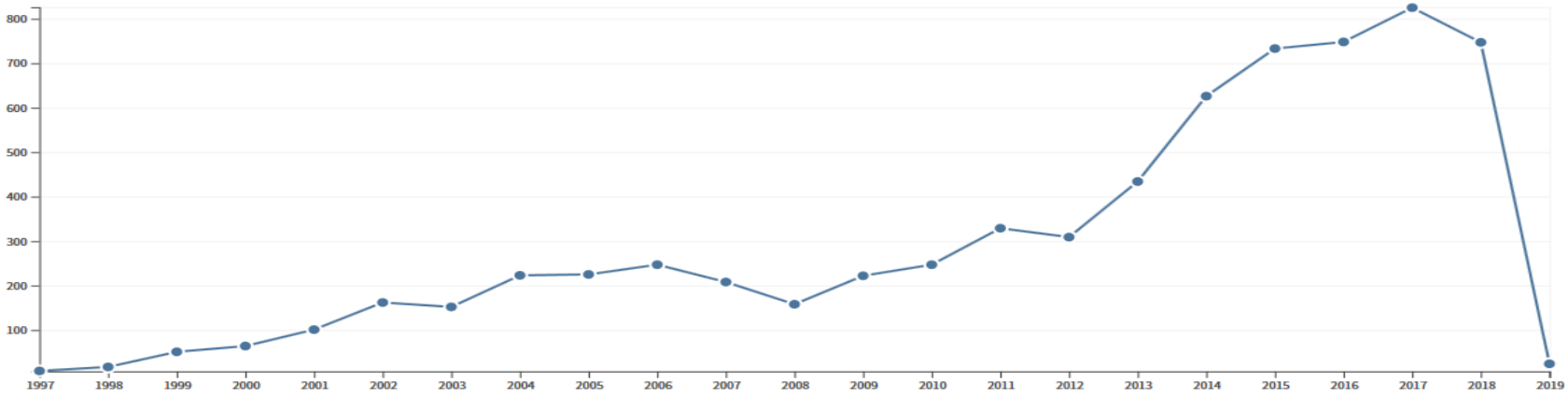
Topic: X-Ray Analysis of Microstresses in Inorganic Composites

1974 – the first paper in Soviet Journal of Crystallography: The crystal structure of $Na_2[(UO_2)SiO_4]$

Till now: 110 publications (90 – in Bar Ilan), 3 patents

Total Publications	*h*-index	Sum of Times Cited	Citing articles
88 Analyze	40	6,860	4,519 Analyze
1999 – 2018	Average citations per item: 77.95	Without self citations: 6,573	Without self citations: 4,449 Analyze

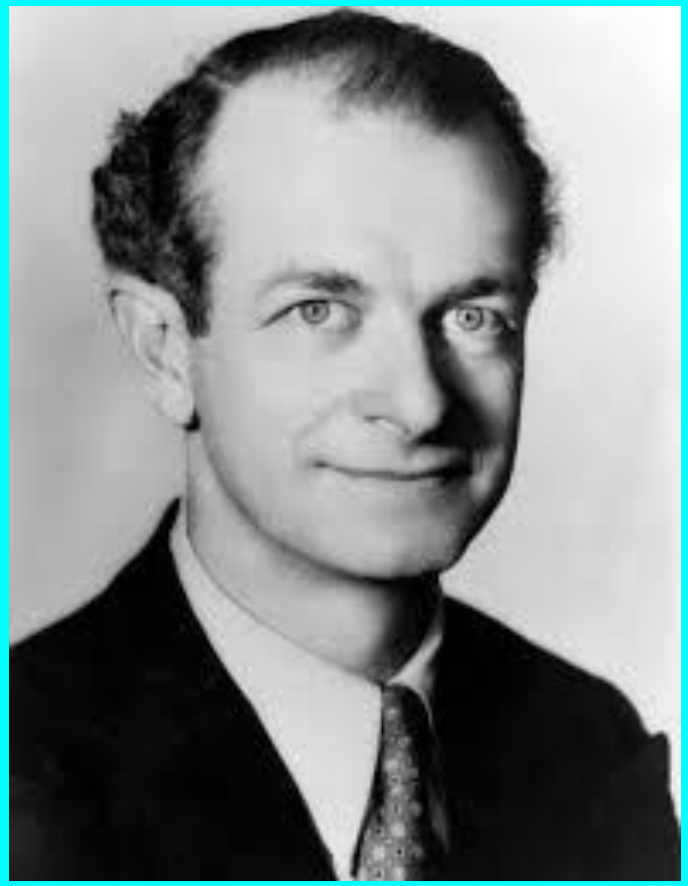
Sum of Times Cited per Year



Old and New Views on the Chemical Bonds: Bond Valence Model for All Types of Chemical Bonds

1. **What is the Bond Valence Model?**
2. **How to calculate the bond order or the bond valence of the chemical bond?**
3. **Can we determine the ion oxidation state from geometry of crystal structure?**
4. **What can be done using the Bond Valence Model?**
5. **Do the main postulates of the Bond Valence Model agree with recent quantum chemistry data?**

Who is the most famous chemist of XX century in the field of chemical bonds?



Ionic
Covalent
Metallic

In 1954 Pauling wined the Nobel Prize in Chemistry, “for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances.”

Bond Valence Model

According to the Pauling's rule of local electroneutrality, the sum of the bond valences around all atoms should be equal to the formal oxidation state, V_i, or to the atomic valence, defined as the number of electrons the *i* atom uses for bonding:

$$V_i = \sum s_{ij}, \qquad (1)$$

where s_{ij} is the valence of the bond between *i* and *j* atoms.

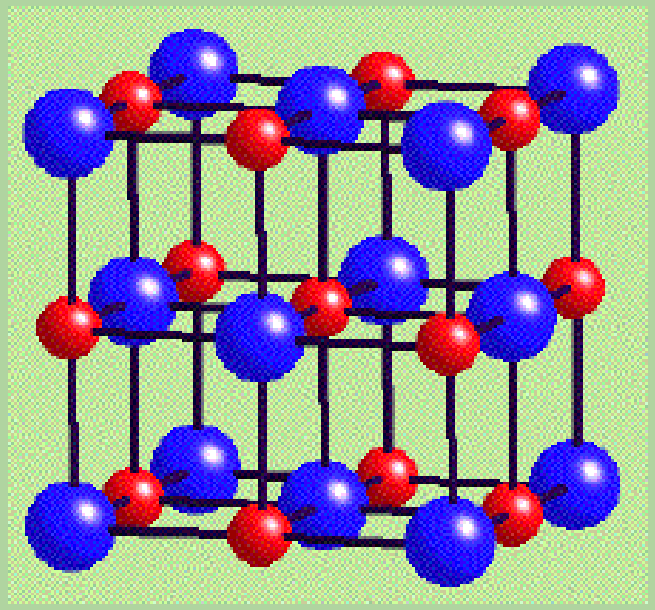
The bond valence is related to the bond length R_{ij} by exponential correlation with empirical constants R_0 and *b* (*b* is commonly equal to 0.37 Å):

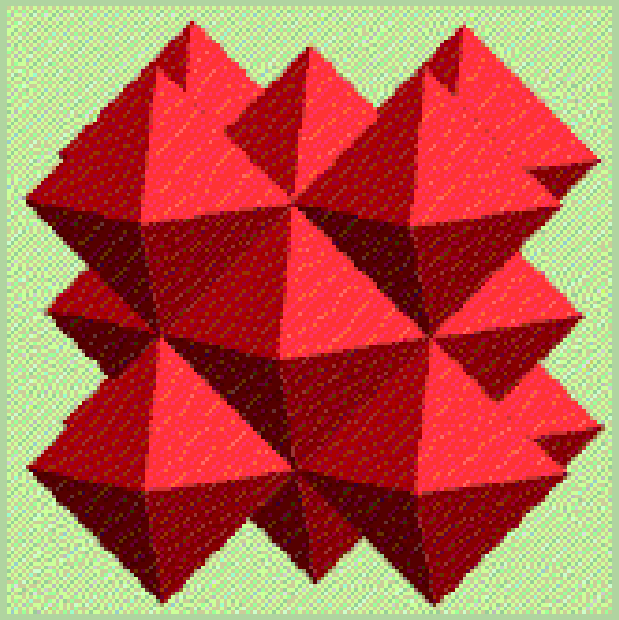
$$s_{ij} = \exp[(R_0 - R_{ij})/b] \qquad (2)$$

It was shown that the tabulated values of R_0 are transferable between the same "cation-anion" pairs in different compounds (R_0 can be regarded as an analogue of the sum of the univalent radii of the cation-anion pairs).

Note that the bond valence model is commonly used for cation-anion pairs.

אלקטרוניטראליות באוקטאהדר [$NaCl_6$]

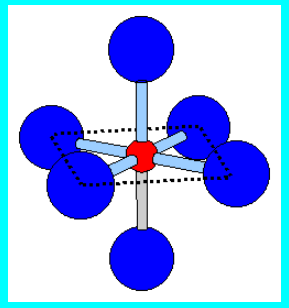




- כל יון Na^+ נמצא בסביבה של שישה יוני Cl^-, כלומר הוא נמצא במרכז האוקטאהדר [$NaCl_6$].
- לכן המטען החיובי במרכז האוקטאהדר שווה ל-1+. (נתרן <u>תמיד</u> בערכיות 1+ בתרכובות)
- כל יון Cl^- משותף לשישה אוקטאהדרי [$NaCl_6$] (קואורדינציה אוקטאהדרלית).
- לכן כל יון Cl^- נותן 1/6 של המטען השלילי שלו לכל אוקטאהדר.
- על מנת לחשב את כל המטען השלילי, יש להכפיל את החלק הזה (1/6) במספר יוני ה Cl^- באוקטאהדר (שש) : 1/6*6=1.
- מסקנה: המטען השלילי שווה בדיוק למטען החיובי.

The difference between formal and effective bond orders

How can we determine the bond order or the bond valence of the chemical bond for a given cation?



Formal bond order or bond valence for a given ion in an ionic compound can be found as the ratio between its formal oxidation state V_i and its coordination number *n*:

$$FBO_{ij} = V_i / n \qquad (1)$$

The effective bond valence can be found in accordance with exponential correlation:

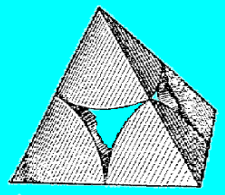
$$s_{ij} = \exp[(R_0 - R_{ij})/b] \qquad (2)$$

R_{ij} is the bond length;
R_0 and *b* are the bond valence parameters, which can be found for each "cation-anion" pair in the Internet Tables.

Example 1: “valence-distance” correlation for the Li-O bonds

$s_{Li\text{-}O} = \exp[(R_0 - R_{Li\text{-}O})/b]$

$R_{0\,Li\text{-}O} = 1.466$ Å, b = 0.37 Å

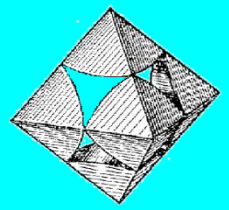


Li_2O

Formal bond order of the Li-O bond is ¼

The real Li-O distance in Li_2O is 1.996 Å.

The effective bond order is 0.24 v.u.



$LiCoO_2$

Formal bond order of the Li-O bond is 1/6

The real Li-O distance in $LiCoO_2$ is 2.092 Å.

The effective bond order is 0.18 v.u.

In most of the solids the effective bond order of the “cation-anion” bonds, which can be found from the exponential correlation, is very close to the formal bond order.

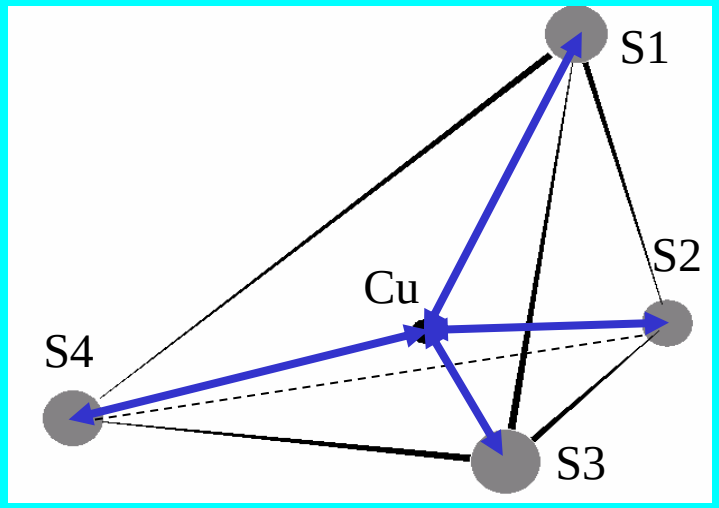
Example 2: Bond valence analysis for Cu atom in Chevrel phase: determination of the oxidation state of the Cu atom

$Cu_2Mo_6S_8$

Bond	Distance	Bond valence
Cu-S1	2.319	0.289
Cu-S2	2.345	0.267
Cu-S3	2.381	0.245
Cu-S4	2.457	0.199
		BVS = 1.00

$$s_{Cu\text{-}S} = \exp[(R_0 - R_{Cu\text{-}S})/b]$$

$R_{Cu\text{-}S}$ = 1.86 Å, b = 0.37 Å



- **Bond valence model is a part of the crystallographic programs that verify the crystal structure solution.**

What can be done using the Bond Valence Model?

1. **Verify the crystal structure determination.**
2. **Determine the ion oxidation state.**
3. **Explain peculiarities of ionic transport.**
4. **Estimate the lattice strains and understand the origin of material instability.**
5. **Explain peculiarities of compounds with metal-metal bonds.**
6. **The BVM is successfully used in accurate molecular dynamics simulations for perovskite or computation of atomic charges in metal organic framework.**

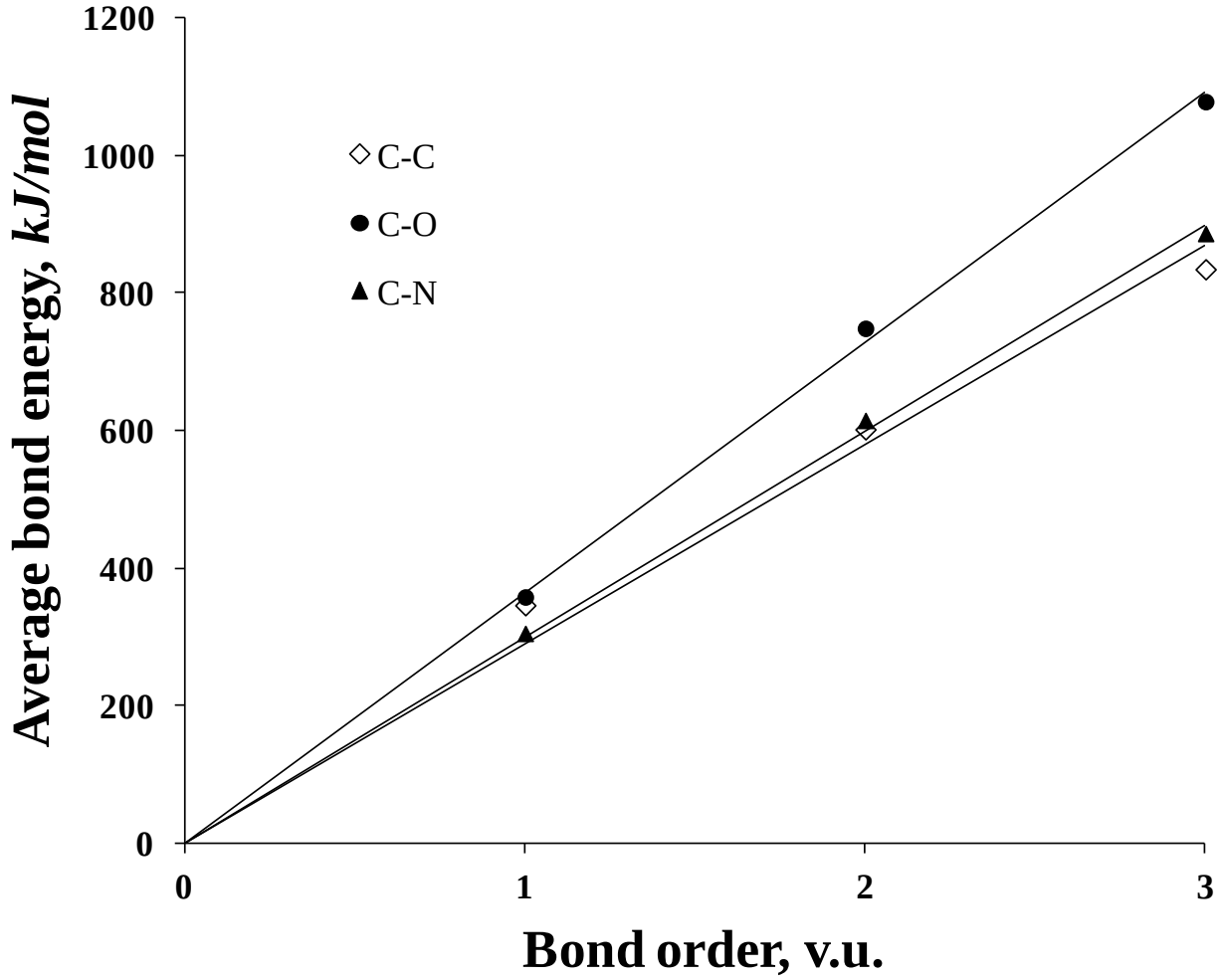
Typical negative referee comment on our work:

- **Instead of using modern quantum chemistry methods, the authors used empirical, old-fashioned model, too general and rough.**

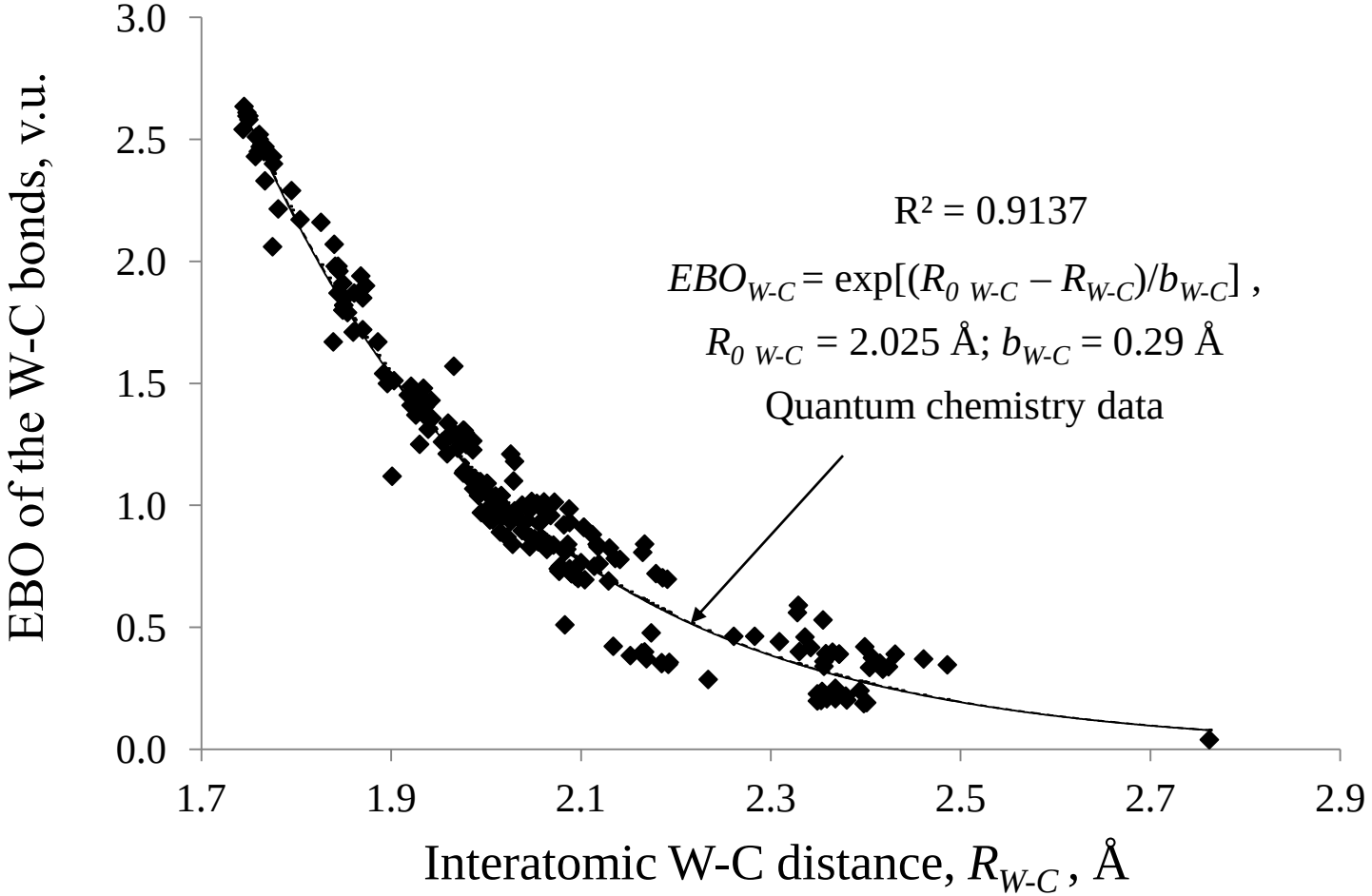
Thus, we decided to clarify the following question:

What is the relationship between the bond orders calculated by the Pauling model and by quantum chemistry methods?

Direct correlation between bond order and the average bond energy for three important atom pairs (The data from G. B. Kaufman, *Inorganic chemistry: principles of structure and reactivity*, ACS Publications, 1993).

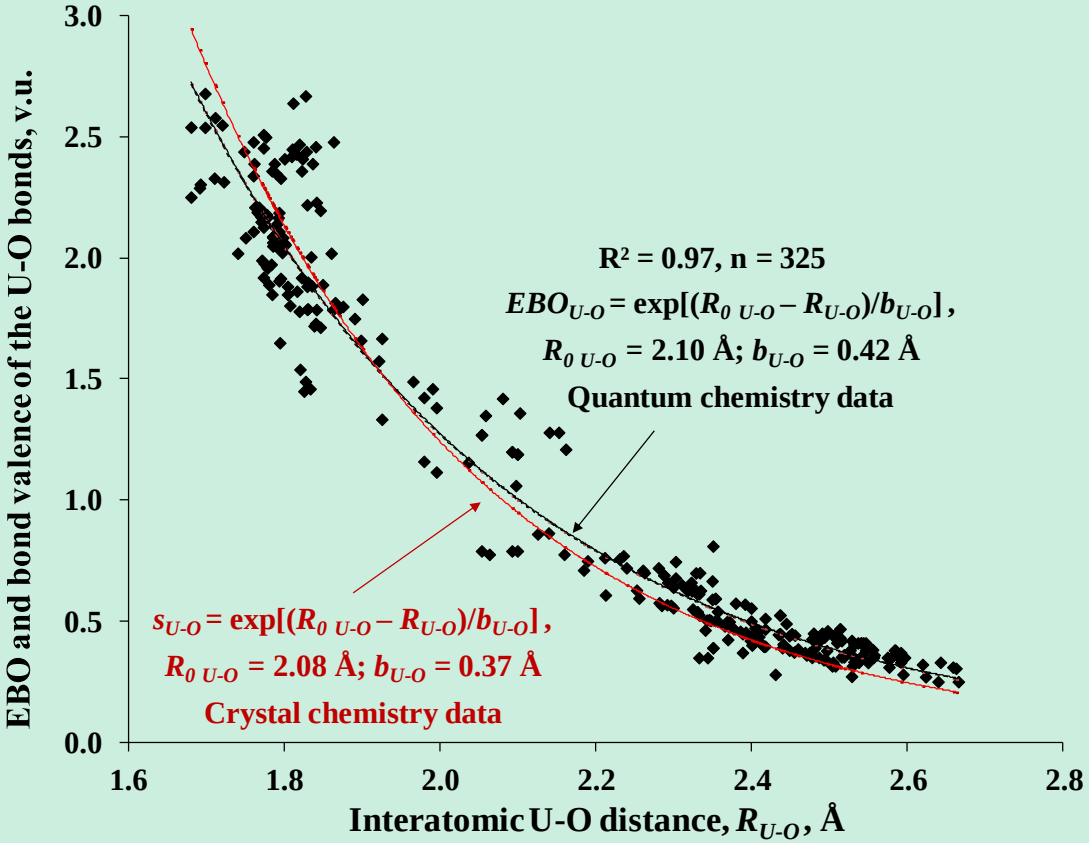


Effective bond orders obtained by quantum chemistry methods

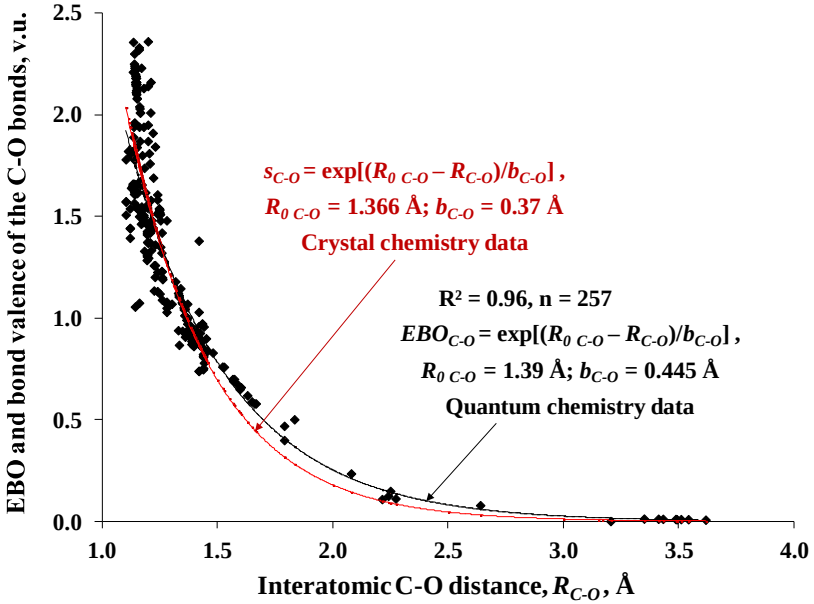


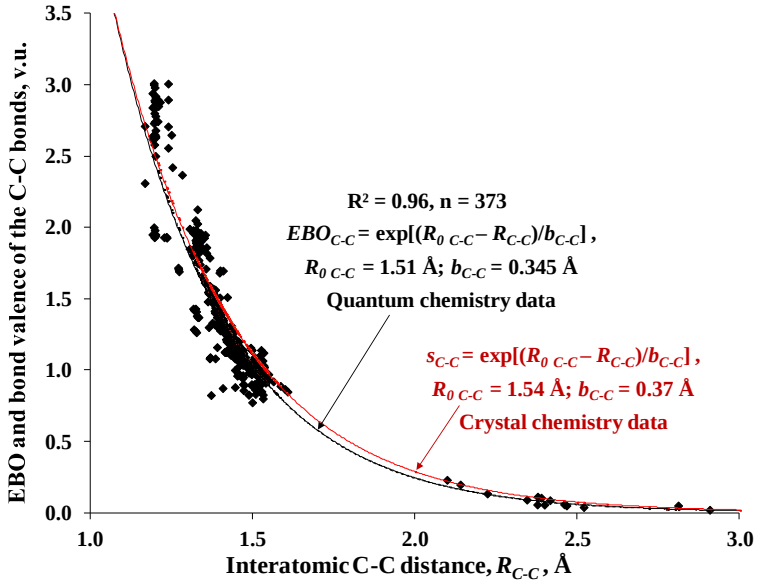
- **In quantum chemistry there are many different methods to determine effective bond order (Wiberg, Mayer BOs, delocalization indices (DI) *etc*.**
- **The data obtained for the same compounds by different quantum chemistry methods give high *BO* dispersion.**
- **This is not surprising, because it is known that these methods are not so accurate.**

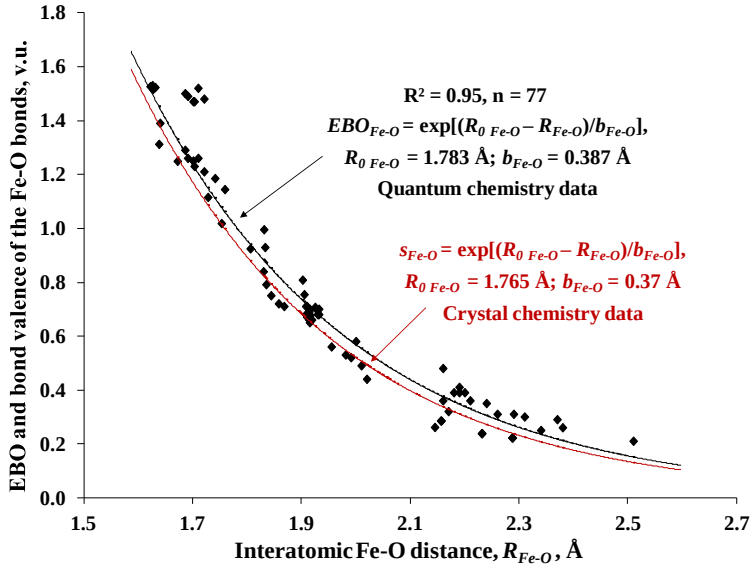
Comparison of quantum chemistry and crystal chemistry curves

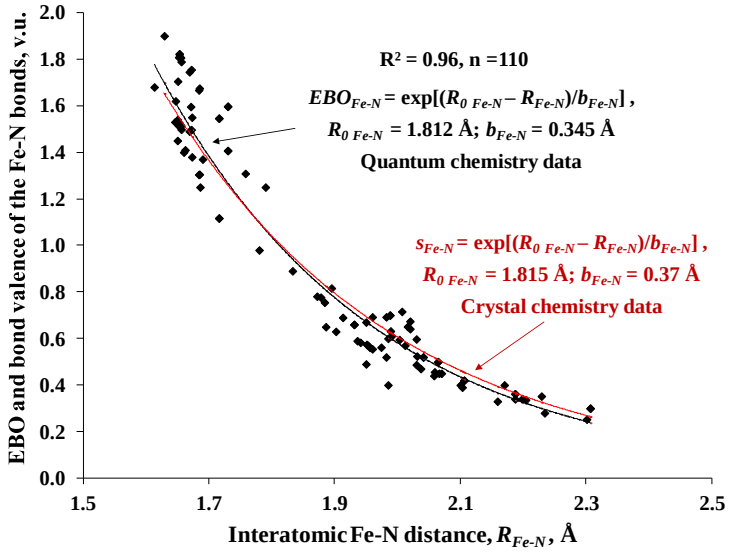


- **In spite of the high dispersion, the quantum chemistry data agree well with exponential correlation.**
- **In the same graph you can see also the exponential curve (in red) accepted in crystal chemistry for the U-O pair.**
- **Note that this curve and the quantum chemistry one are very close to each other.**
- **The difference does not exceed the dispersion of quantum chemistry data, confirming the validity of the *Bond valence model*.**


EBO and bond valence of the C-O bonds, v.u.
Interatomic C-O distance, R_{C-O}, Å
$s_{C-O} = \exp[(R_{0\ C-O} - R_{C-O})/b_{C-O}]$,
$R_{0\ C-O}$ = 1.366 Å; b_{C-O} = 0.37 Å
Crystal chemistry data
R² = 0.96, n = 257
$EBO_{C-O} = \exp[(R_{0\ C-O} - R_{C-O})/b_{C-O}]$,
$R_{0\ C-O}$ = 1.39 Å; b_{C-O} = 0.445 Å
Quantum chemistry data


EBO and bond valence of the C-C bonds, v.u.
Interatomic C-C distance, R_{C-C}, Å
R² = 0.96, n = 373
$EBO_{C-C} = \exp[(R_{0\ C-C} - R_{C-C})/b_{C-C}]$,
$R_{0\ C-C}$ = 1.51 Å; b_{C-C} = 0.345 Å
Quantum chemistry data
$s_{C-C} = \exp[(R_{0\ C-C} - R_{C-C})/b_{C-C}]$,
$R_{0\ C-C}$ = 1.54 Å; b_{C-C} = 0.37 Å
Crystal chemistry data

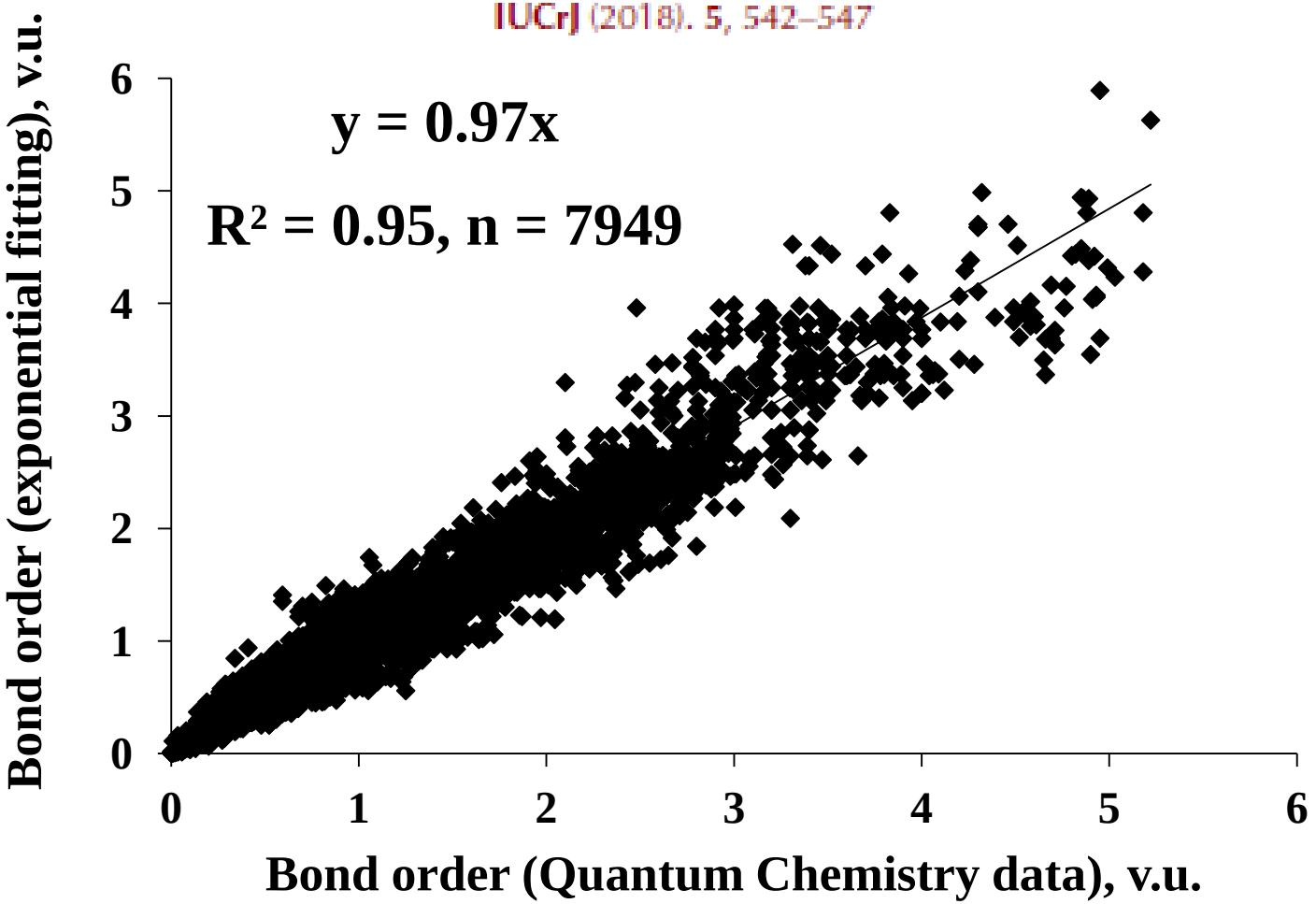

EBO and bond valence of the Fe-O bonds, v.u.
Interatomic Fe-O distance, R_{Fe-O}, Å
R² = 0.95, n = 77
$EBO_{Fe-O} = \exp[(R_{0\ Fe-O} - R_{Fe-O})/b_{Fe-O}]$,
$R_{0\ Fe-O}$ = 1.783 Å; b_{Fe-O} = 0.387 Å
Quantum chemistry data
$s_{Fe-O} = \exp[(R_{0\ Fe-O} - R_{Fe-O})/b_{Fe-O}]$,
$R_{0\ Fe-O}$ = 1.765 Å; b_{Fe-O} = 0.37 Å
Crystal chemistry data


EBO and bond valence of the Fe-N bonds, v.u.
Interatomic Fe-N distance, R_{Fe-N}, Å
R² = 0.96, n =110
$EBO_{Fe-N} = \exp[(R_{0\ Fe-N} - R_{Fe-N})/b_{Fe-N}]$,
$R_{0\ Fe-N}$ = 1.812 Å; b_{Fe-N} = 0.345 Å
Quantum chemistry data
$s_{Fe-N} = \exp[(R_{0\ Fe-N} - R_{Fe-N})/b_{Fe-N}]$,
$R_{0\ Fe-N}$ = 1.815 Å; b_{Fe-N} = 0.37 Å
Crystal chemistry data

Do the basic crystal chemistry principles agree with a plethora of recent quantum chemistry data?

Elena Levi, Doron Aurbach and Carlo Gatti

IUCrJ (2018). 5, 542–547



- **Using a huge number of quantum chemistry data we showed that the exponential correlations are valid for any types of chemical bonds.**

Comparison between recent quantum chemistry methods and the old Pauling model

Which method needs more efforts?

Quantum chemistry methods	Bond valence model
Expensive, need many hours of calculations, commonly used for small molecules	Zero cost, needs only a few minutes of work in EXEL, and can be used for any complex compound.

Which method is more accurate?

Quantum chemistry methods	Bond valence model
The dispersion of quantum chemistry values is very high	The results should be much more accurate if we will use the exponential correlations