Discovering correlations in the interatomic distances of inorganic crystals

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Introduction
We consider the crystal structures databases (ICSD and COD), and we compute and analyze the interatomic distance distribution for element pairs which have enough structures. In general, the distance distribution can be divided into three parts: covalent bond region, van der Waals region and gap between them.

The covalent peak and the gap between bond and non-bond regions are detected based on a peak finding algorithm and detection of a minimum in the distribution. A set of covalent radii for 83 elements together with threshold distances for separating bond and non-bond regions are obtained from the statistical analysis using the least-square method.

These two sets of radii both show periodic trends. The periodic trend:

\[ r_{i} + r_{j} + \sigma \leq d_{\text{range}} \leq r_{i} + r_{j} + \sigma/2 \]

Where \( r_{i}, r_{j} \) are the covalent radii from Cordero and constant \( \sigma \) is 0.5 Å.

The peak at the largest distance would be chosen as the covalent peak due to the multiple bonds (C-O) and different oxidation states (Mn-O) as shown in Fig. A and Fig. B.

Methods
We compute the interatomic distance distribution as follows:

**Supercell creation:**
- Calculate the central point of the unit cell \( P_{c} \), the maximum distance \( r_{\text{max}} \) between \( P_{c} \) and all the atoms in the unit cell and the minimum distance \( r_{\text{min}} \) between \( P_{c} \) and the faces of the unit cell.
- Calculate the number \( n \) of repetition of the unit cell in each dimension as:
  \[ n = \lceil \frac{r_{\text{max}} - r_{\text{min}}}{P_{c}} \rceil \times 2 + 1 \]
  Where \( \lceil \cdot \rceil \) represents the ceiling function \( \lceil x \rceil \) which gives the smallest integer \( \geq x \) and \( r_{c} \) is the cutoff distance which is the maximum distance used in searching.

**Filtering out symmetry redundant pairs:**
For each symmetry-invariant atom in the central unit cell, we pick all the atoms located within the sphere of radii \( r_{c} \) centered in this atom, and compute all the distance from it.

Two reasons for that:
- Due to the periodicity of the crystal, other atoms which are not in the central unit cell are copies of those in the central unit cell.
- Symmetry-invariant atoms in the central unit cell would provide unique distance information and avoid repeated pair distances from the atoms which have the same Wyckoff position.

**Statistical analysis using the least-square method and detection of a minimum in the distance,**
which gives the smallest integer \( \geq x \) and \( r_{c} \) is the cutoff distance.

**Comparison with previous result:**
- Proposed covalent radii are almost same as those from Cordero and larger than ones from Pyykkö.
- On average, each threshold distance is 0.63 Å shorter than the corresponding vdW radii from Alvarez.

**Absolute error:**
Absolute error between sum of two proposed threshold distances and detected gap range (0 represents sum of two distances falls into the detected gap).

**Conclusion**
- Present a method to calculate the distance distribution in a database of crystal structures.
- By using a least-square method, peak finding algorithm and detection of a minimum in the distance, two set of radii (covalent radii and threshold distances) can be obtained.
- The sum of the two threshold distances can be used as a rough condition to separate bonding and non-bonding regions.

**References**