Derivation of a Covalent Radii Table From Open Crystallographic Data

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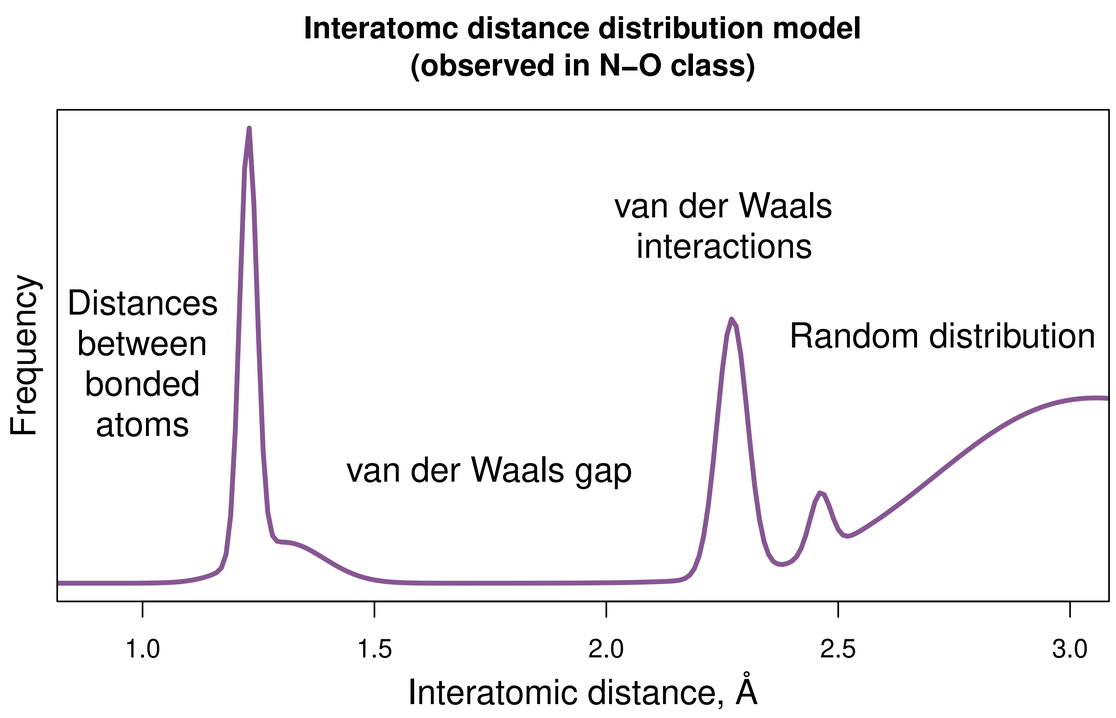
Introduction

X-ray crystallography is able to determine the exact positions of atoms that constitute crystal structures [1], but cannot capture chemical bonding. Due to this, bonding is often determined using a heuristic which considers two atoms to be connected if the calculated distance between them is less or equal to the sum of their covalent radii. This distance is called a covalent bond length.

Motivation

- Most popular covalent radii tables [2, 3, 4] are derived using data from proprietary databases that restrict the usage and spread of such derivative datasets.
- There is a need to develop an independent workflow that allows covalent radii tables to be automatically calculated and ensures reproducibility of the results.

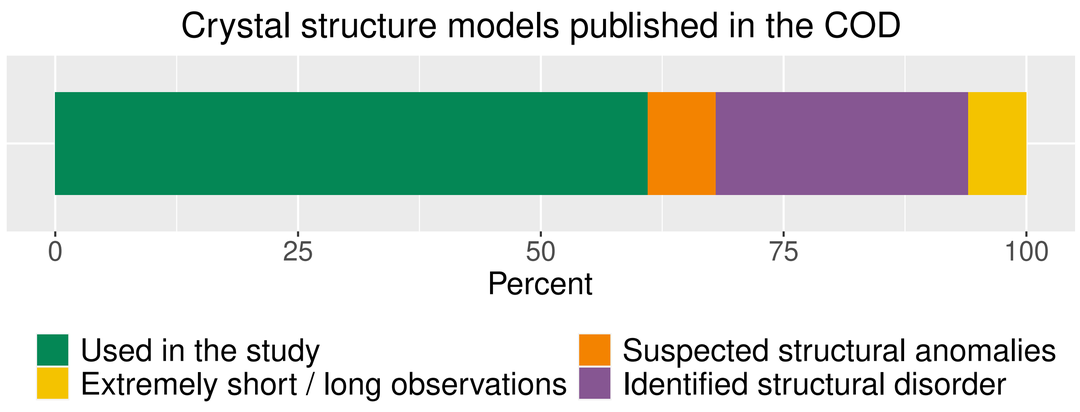
Interatomic distance distribution



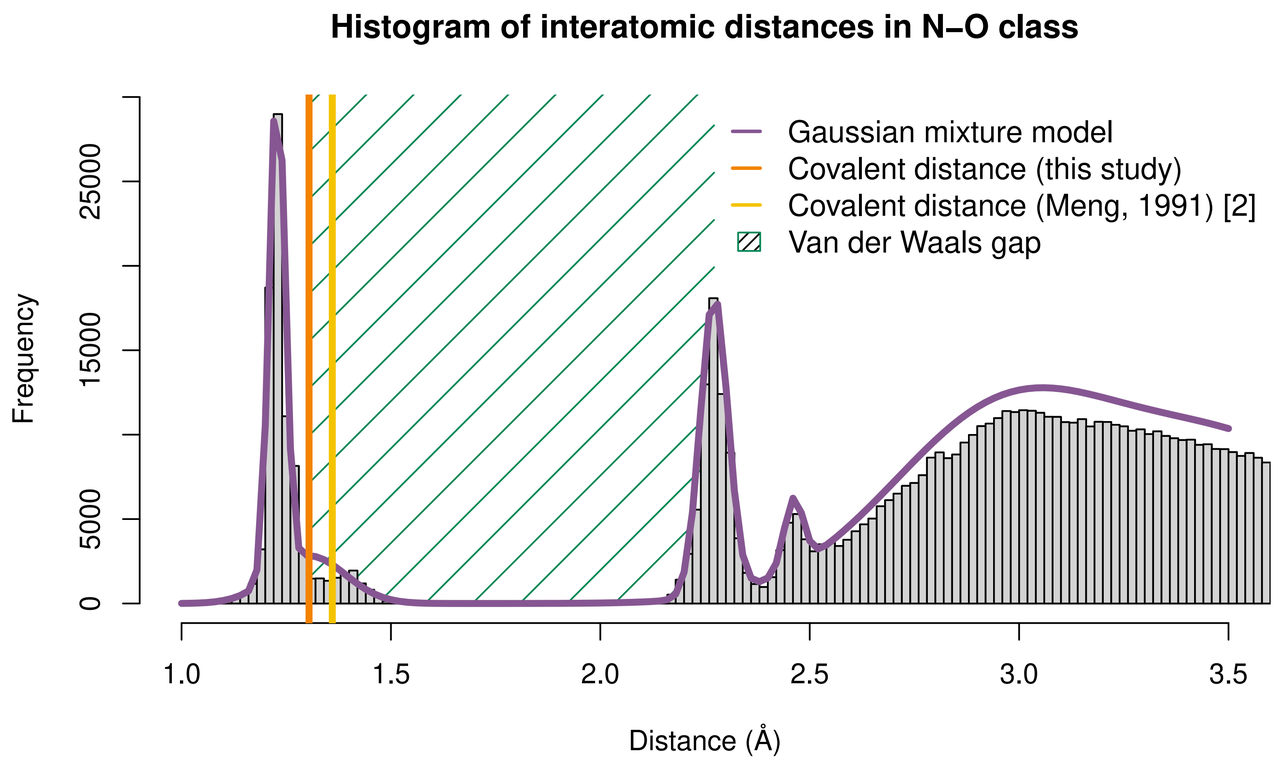
- All interatomic distance observations are classified based on chemical elements between which the distance was measured.
- Van der Waals gap is an interval that separates peaks formed by covalent interactions from those formed mainly by van der Waals interactions [5].
- Interatomic distance distribution can be approximated by a Gaussian mixture model [5].

Data and filtering

- 485 000 entries from the Crystallography Open Database (COD) [6] were analyzed.
- Crystallographic models need to be filtered to ensure that only realistic distances between atoms are used in the study.

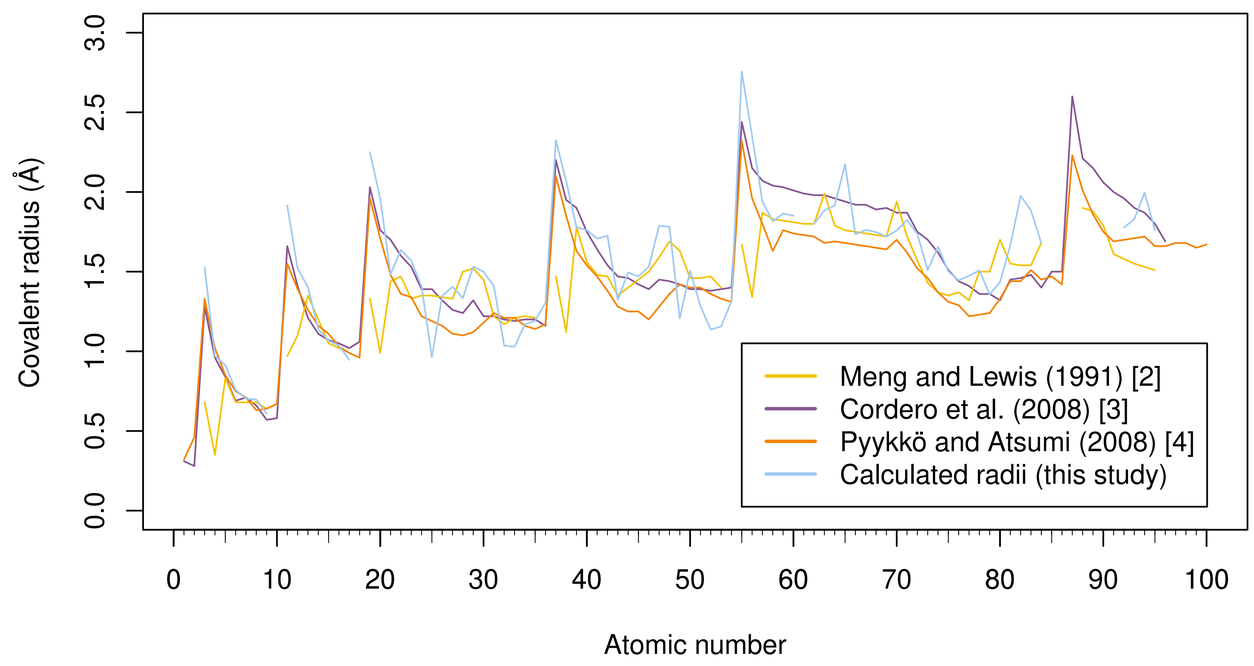


Derivation of covalent radii values



- Method uses the best fitting Gaussian mixture model per Bayesian Information Criterion [7].
- Each pair of neighbouring components is examined to find the lowest density region in the distribution, which corresponds to be the van der Waals gap.
- Mean of the component preceding the van der Waals gap is selected as the maximum covalent bond length for each atom distance class.

Derived covalent radii table



- Derived covalent radii values follow expected distribution trend based on the atomic number.

Conclusions

- Methodology for automated covalent radii derivation was developed.
- Derived covalent radii table is freely accessible online (via QR code on the left).
- Further research will be focused on testing the derived covalent radii through real molecule connectivity validation.

Bibliography

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