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Crystal Structure Prediction by Vertex Removal in Euclidean Space

Duncan Adamson, Argyrios Deligkas, Vladimir V. Gusev and Igor Potapov
University of Liverpool, Department of Computer Science
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What is a *Crystal*?

- **Crystals** are a fundamental type of material structure.
- Each crystal is composed of charged particles called ions.

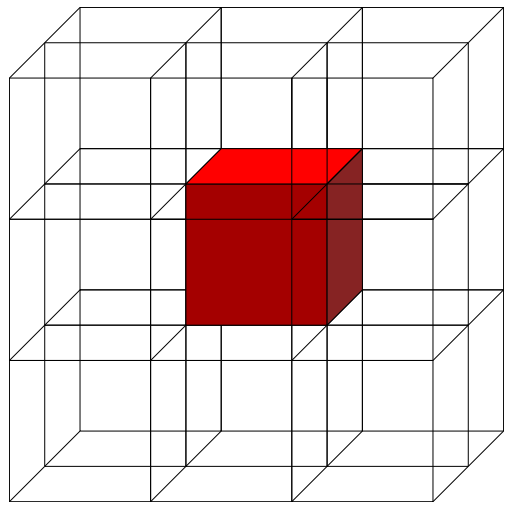

Figure 1: Unit cell highlighted in red, note any other box would be equivalent

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- **Crystals** are a fundamental type of material structure.
- Each crystal is composed of charged particles called ions.
- We consider crystals to be made up of unit cells.
- Each unit cell is the smallest repeating region of space within the crystal.
- As far as we are concerned, this is infinite.

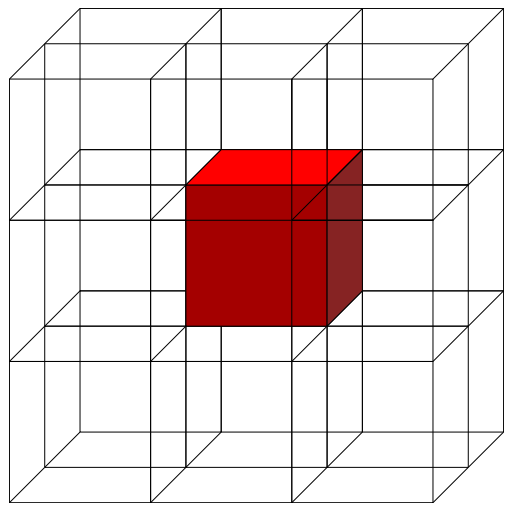


Figure 1: Unit cell highlighted in red, note any other box would be equivalent

What is a *Unit Cell*?

- Each unit cell is a collection of Ions.
- This can be thought of as the period of the Crystal.
- We assume each unit cell is **independent** of all other unit cells.
  - This means that we only consider the **interaction** of ions within the same cell.
- Every cell must have a total **Neutral** charge.

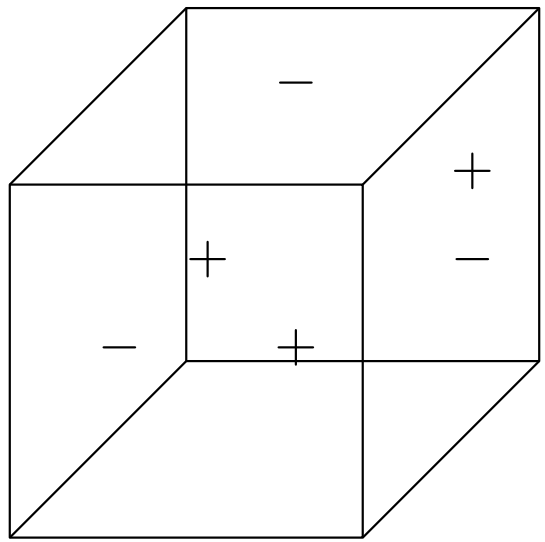


Figure 2: Example of a unit cell

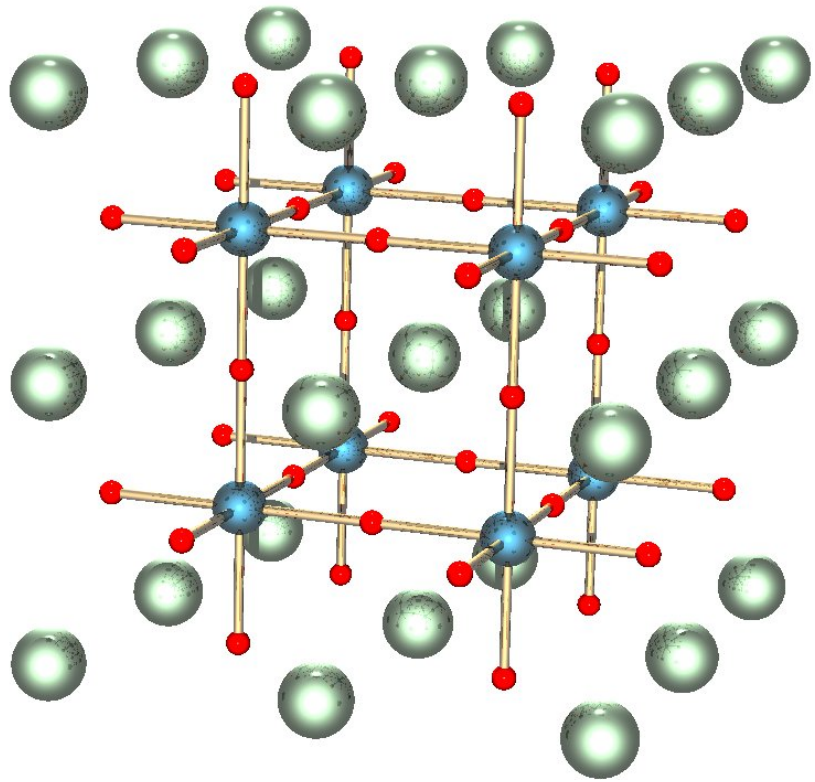
What is an *Ion*?

- A charged point in space belonging to a **specie**.
- The specie determines its interaction with other ions, as well as its charge.
- We denote the charge of ion i as q_i.
- The sum of the charges must be 0, i.e.:

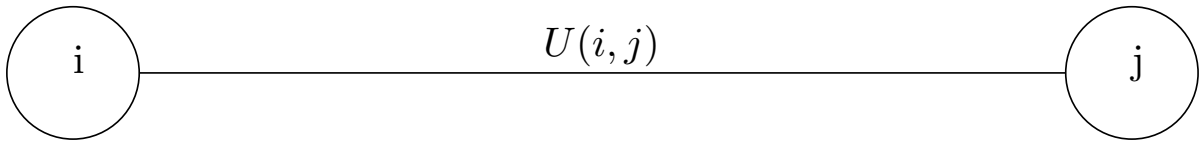
$$\sum_{i \in S} q_i = 0.$$

Strontium Titanate ($SrTiO_3$)

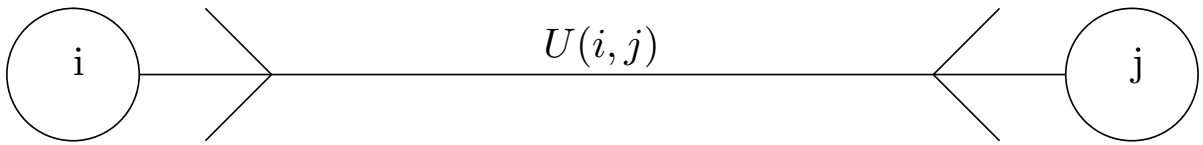
Ion	Charge
Sr	+ 4
Ti	+ 2
O	- 2



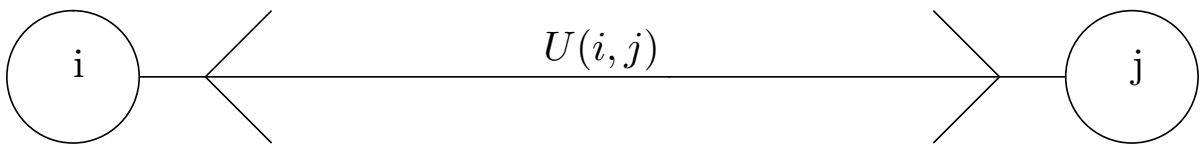
How do we determine potential energy between ions?



- We define the pairwise interaction for any pair of ions by some function $U(i,j)$.
- This is parameterised by the species of the ions and the distance between them.

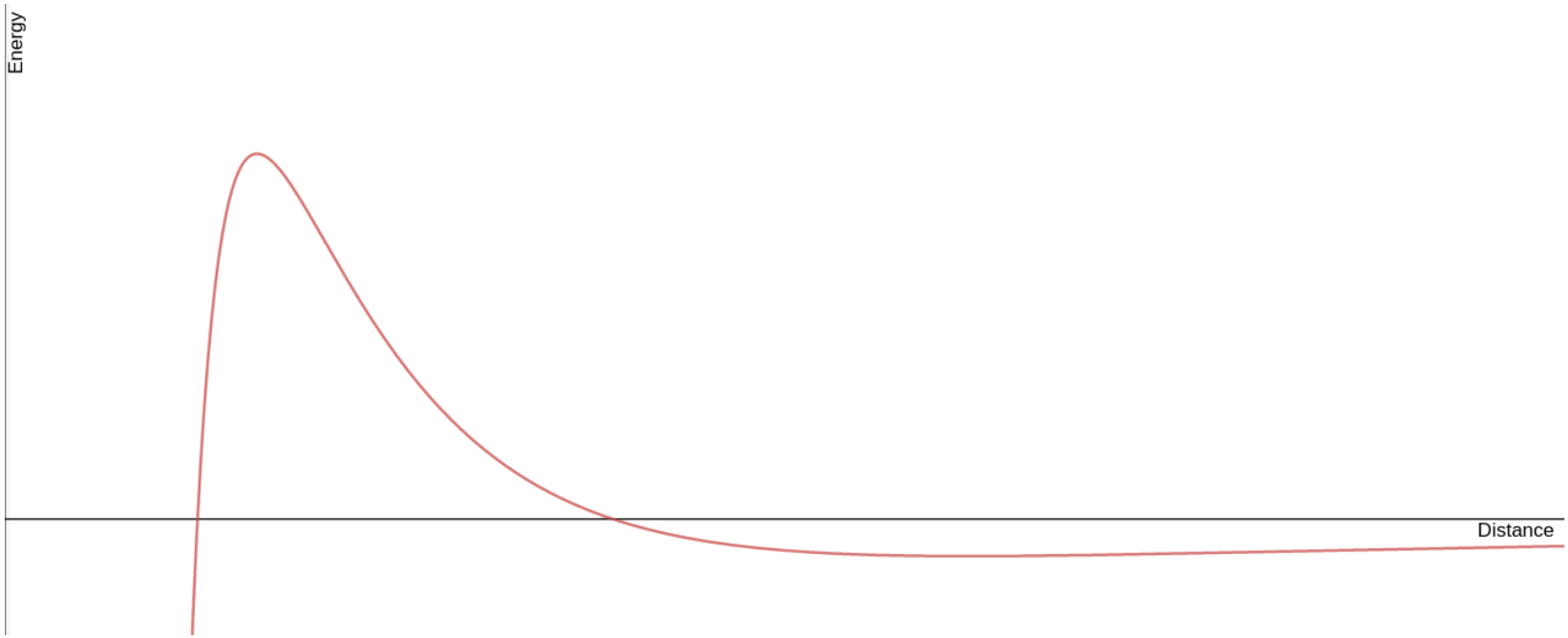


- A negative value for potential means that the ions are trying to move closer together, which implies the crystal will be stronger.



- A positive value means that the ions are repelling each other.

Buckingham-Coulomb potential energy



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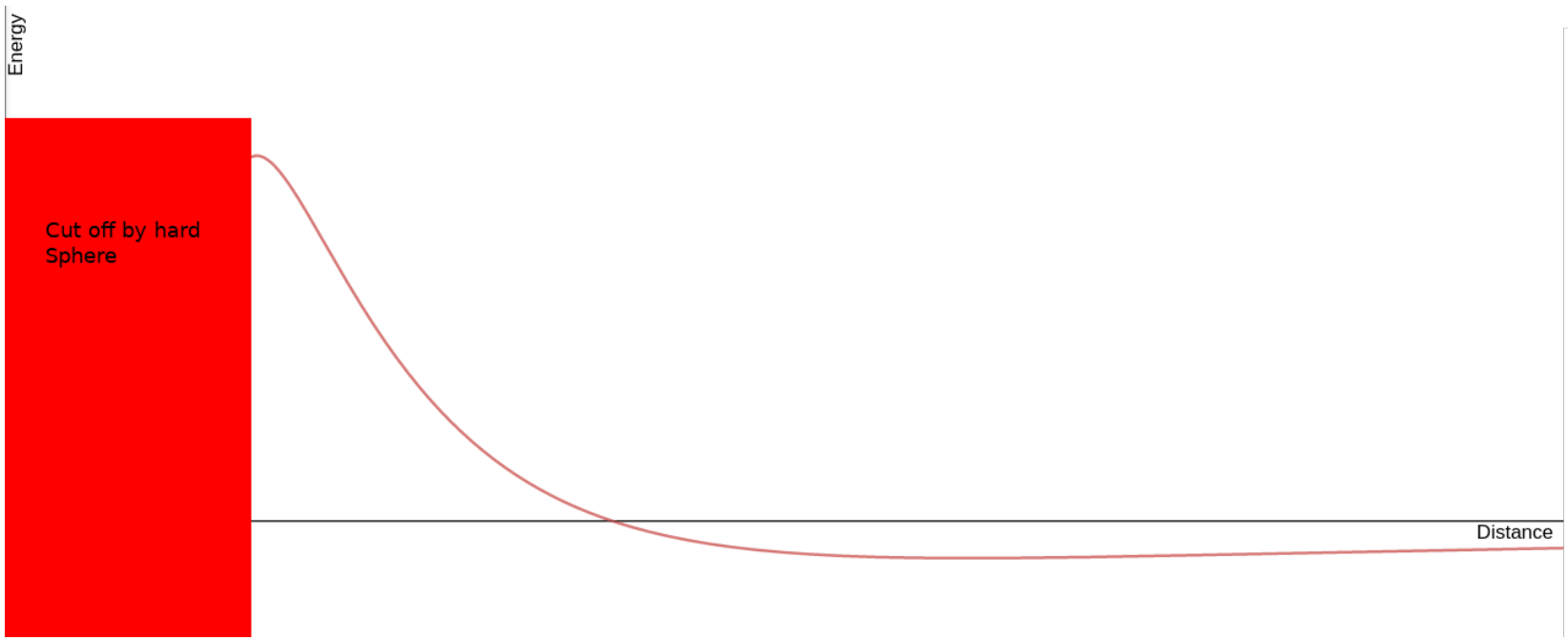

Buckingham-Coulomb potential

- One of the most popular energy functions is the **Buckingham-Coulomb** potential (U^{BC}), which is the sum of the Coulomb potential (U^{C}) and the Buckingham potential (U^{B}).

$$U^{C}(i,j) = \frac{q_i q_j}{r_{ij}}$$

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$$U^{BC}(i,j) = U^{B}(i,j) + U^{C}(i,j) = \frac{A_{ij}}{e^{B_{ij} r_{ij}}} - \frac{C_{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{r_{ij}}$$

$SrTiO_3$ Parameters

- For $SrTiO_3$ we have 18 parameters.
- Note that the parameters going from an Oxygen to a Strontium are the same as going from a Strontium to an Oxygen.

	Sr	Ti	O
Sr	$A_{Sr,Sr}, B_{Sr,Sr}, C_{Sr,Sr}$	$A_{Sr,Ti}, B_{Sr,Ti}, C_{Sr,Ti}$	$A_{Sr,O}, B_{Sr,O}, C_{Sr,O}$
Ti	$A_{Sr,Ti}, B_{Sr,Ti}, C_{Sr,Ti}$	$A_{Ti,Ti}, B_{Ti,Ti}, C_{Ti,Ti}$	$A_{Ti,O}, B_{Ti,O}, C_{Ti,O}$
O	$A_{Sr,O}, B_{Sr,O}, C_{Sr,O}$	$A_{Ti,O}, B_{Ti,O}, C_{Ti,O}$	$A_{O,O}, B_{O,O}, C_{O,O}$

What is Crystal Structure Prediction?

- Crystal Structure Prediction is predicting the structure of crystals.
- To formulate this as a problem, we must define what a crystal is, and what makes a good structure.
- Crystals are made of **ions** with a potential energy between them, represented by unit cells.
- We want a negative potential energy whenever possible.
    - The more negative, the better.

Crystal Structure Prediction

Problem *Crystal Structure Prediction* (CSP)
Input: A multiset of ions, A, an area of space, C.
Output: An arrangement, S, made by placing some copies of the ions in A in C, with a **neutral** charge **minimising** the energy between the ions.

Crystal Structure Prediction

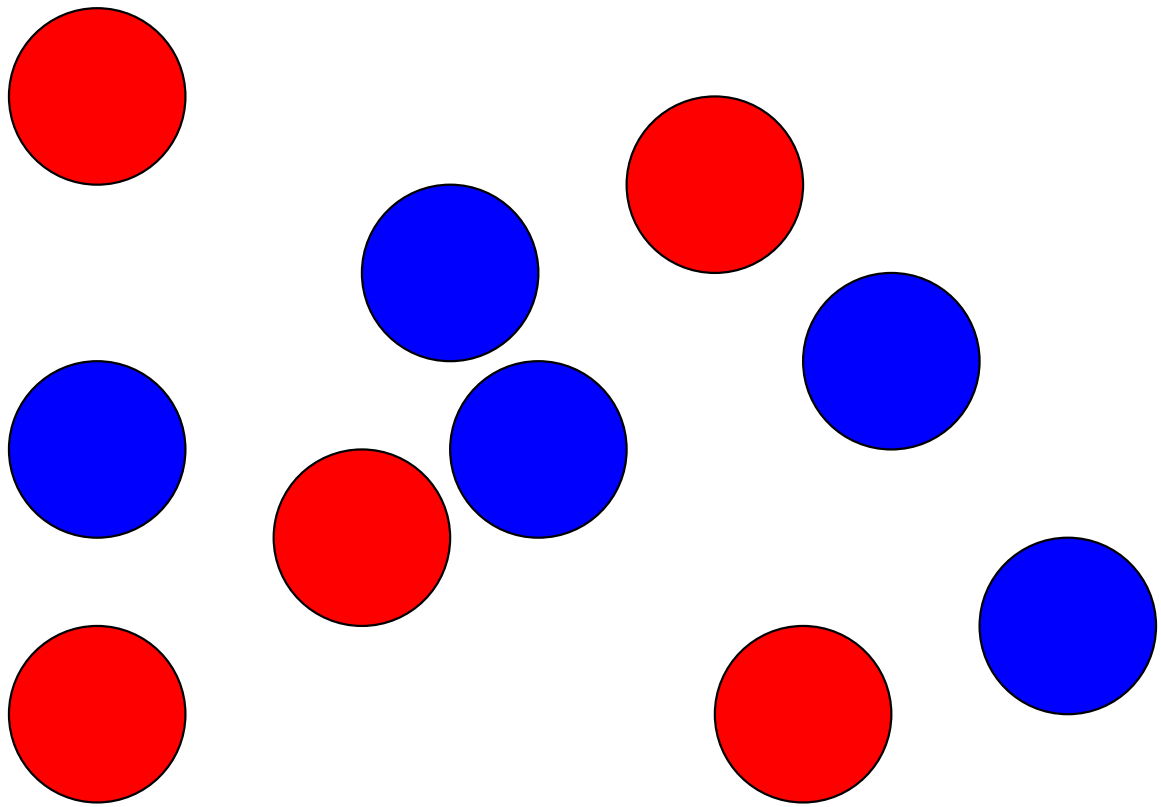
- This problem has been claimed to be NP-Hard, without any correct formal proof.
- There are results for related problems, such as finding solutions to the magnetic partition function [1].
- There have also been heuristic approaches, however these do not provide any guarantees on correctness.

[1] F Barahona, On the computational complexity of ising spin glass models. *Journal of Physics A: Mathematical and General*, 15(10):3241–3253, oct 1982

Our Approach

- Considering only a single simple operations will be easier to reason about.
- Our goal is to create a larger set of operations which we understand.
- The first of these will be the removal operation.
- **Idea:** Create a highly dense initial arrangement of ions, then remove ions from it to make a feasible crystal structure.
- We will assume our initial structure is neutral.

Our Approach



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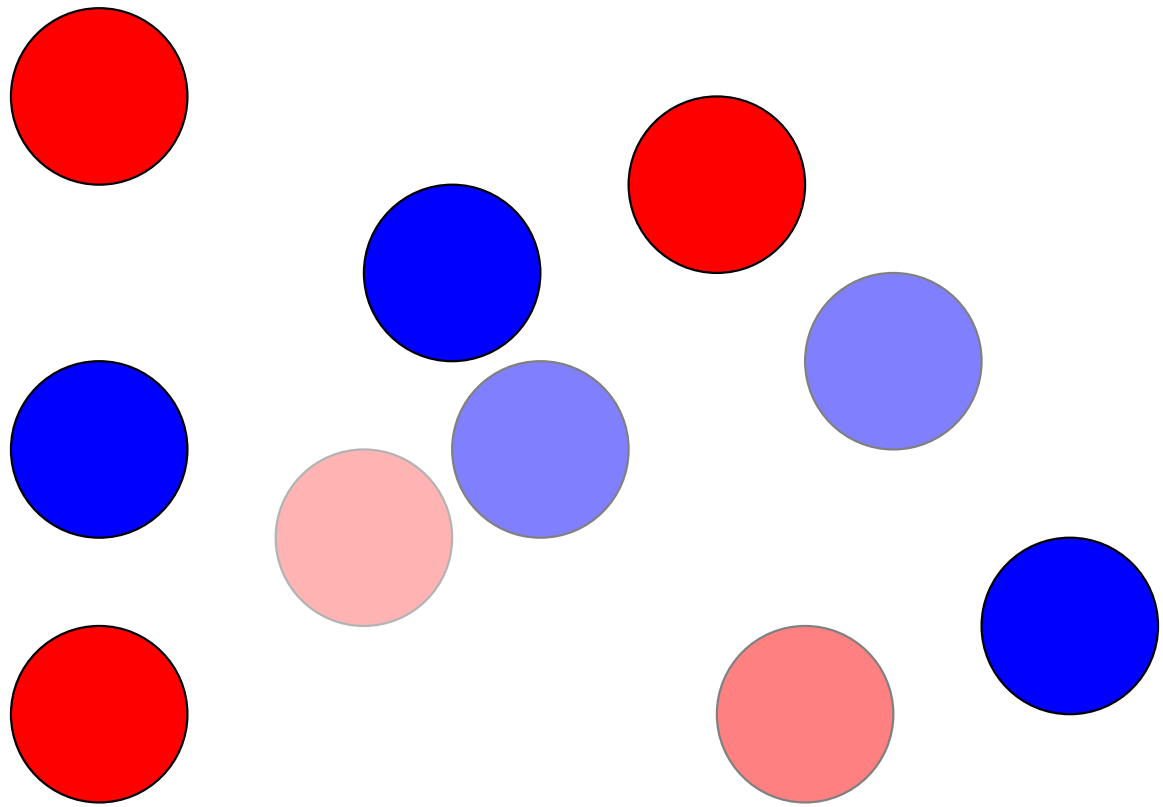

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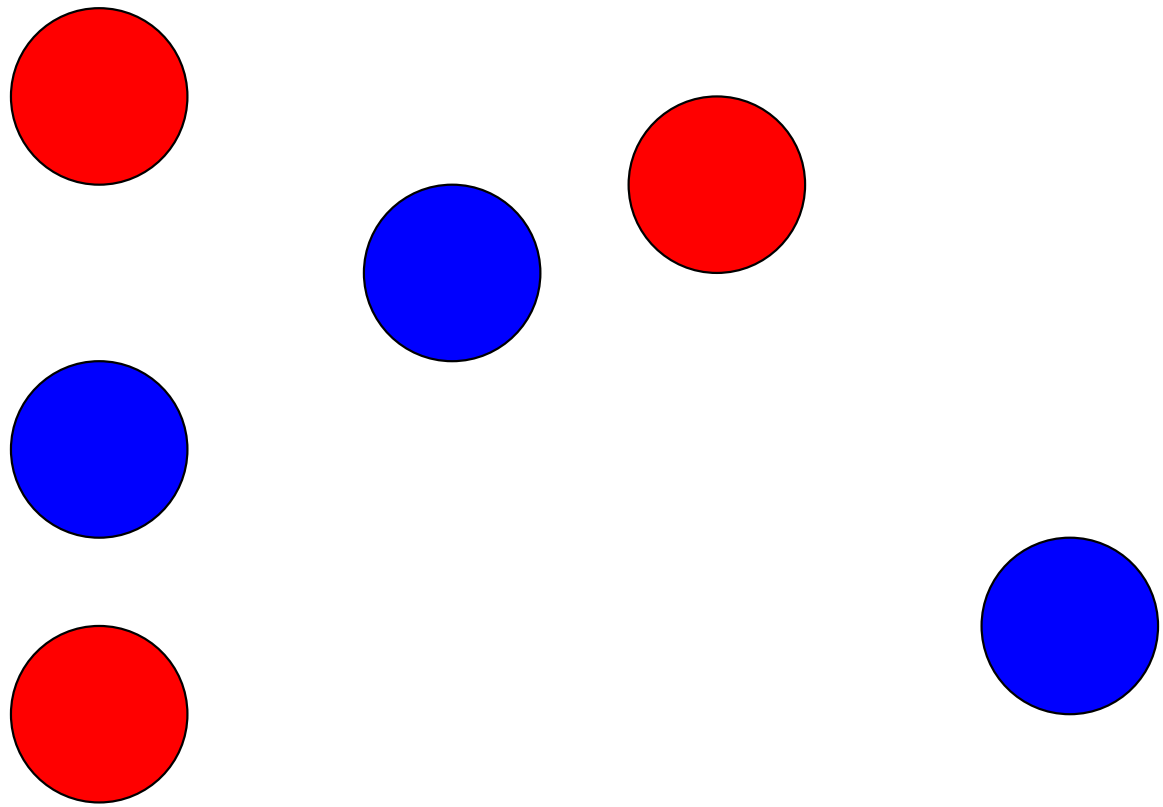

Crystal Structure Prediction by Vertex Removal

Problem	*Optimal Minimal K-Charge Removal* (K-CHARGE REMOVAL).
Input	A structure of ions, S, a pairwise energy function, U, and an integer k.
Output	A minimal removal of k charges from S such that the total energy is minimised.

Modelling problems in 3D Euclidean Graphs

- Embedding problems into a weighted 3d euclidean graph is hard.
- A lot of preprocessing is required.
  - In many cases this may surmount to finding the solution!
- For k-charge removal this is further complicated by the charges.

What do we want to prove?

- To understand this problem better, we want to find out what the complexity is for this problem.
- We want to find this for both the general case, and for the more restricted case for **realistic** instances, where we have:
  - A limited number of species of ions
  - Charges limited to "small" values, ideally ± 1

Our Results

Energy	Charges	Species	Result
U^{BC}	± 1	Unrestricted	NP-Hard, Cannot be approximated in polynomial time within a factor of $n^{1-\epsilon}$ for $\epsilon > 0$ (unless P $=$ NP)
$\mathbf{U^{BC}}$	$\mathbf{\pm 1}$	**2**	**NP-Hard**
U^{C}	Unrestricted	Unrestricted	NP-Hard

Restriction to 2 Species

- The fewest number of species we can have in a structure is two, one for the positive ions and one for the negative ions.
- We want to show that the problem remains NP-Complete under this restriction.
- For this we will reduce from the **Independent Set** problem on **penny graphs**.

Penny graphs

Figure 3: By David Eppstein - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=56426404

Conversion to K-CHARGE REMOVAL

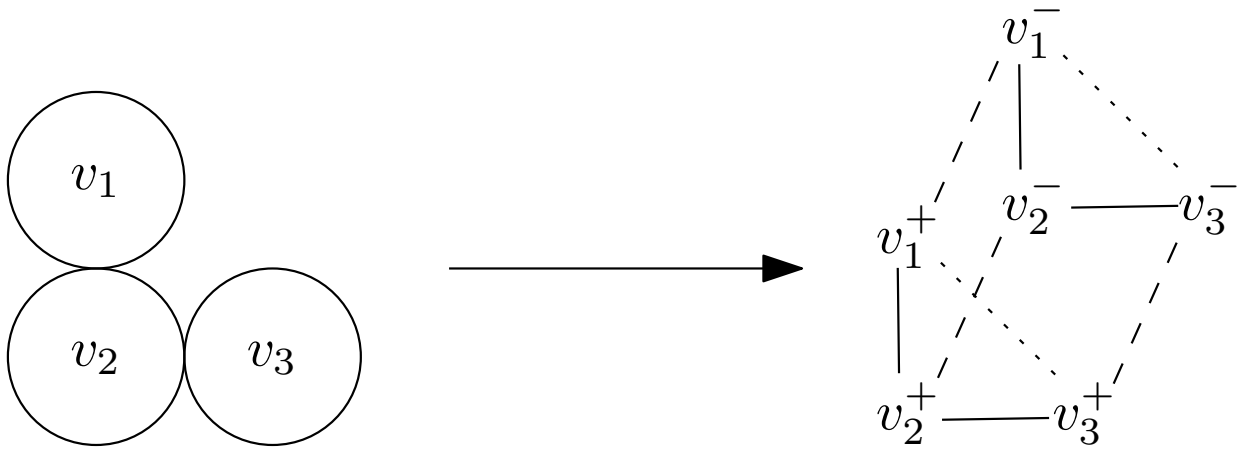

Figure 4: We place ions at the centre positions of each penny.

Overview of Penny Graphs to k-Charge Removal

- **Idea:** create values so that:
  - The energy between the pair of ions representing a single vertex is -1.
  - The energy between pairs representing adjacent ions is greater than 1 (distance r).
  - The energy between non-adjacent ions (distance at least $\sqrt{2}r$) is less than $\frac{1}{n^2}$.
- We claim we can achieve this by taking advantage of the nature of the Buckingham-Coulomb Potential (but will leave the details for further discussion).

Future Work

- Consider the energy beyond just one unit cell.
- Consider the complementary problem of insertion.
- Analyse the state space of all potential unit cells.