UNIVERSITY OF LIVERPOOL

LEVERHULME TRUST

The Leverhulme Research Centre for Functional Materials Design

Crystal Structure Prediction via Oblivious Local Search

Dmytro Antypov, Argyrios Deligkas, Vladimir Gusev, Matthew J. Rosseinsky, Paul G. Spirakis, **Michail Theofilatos**

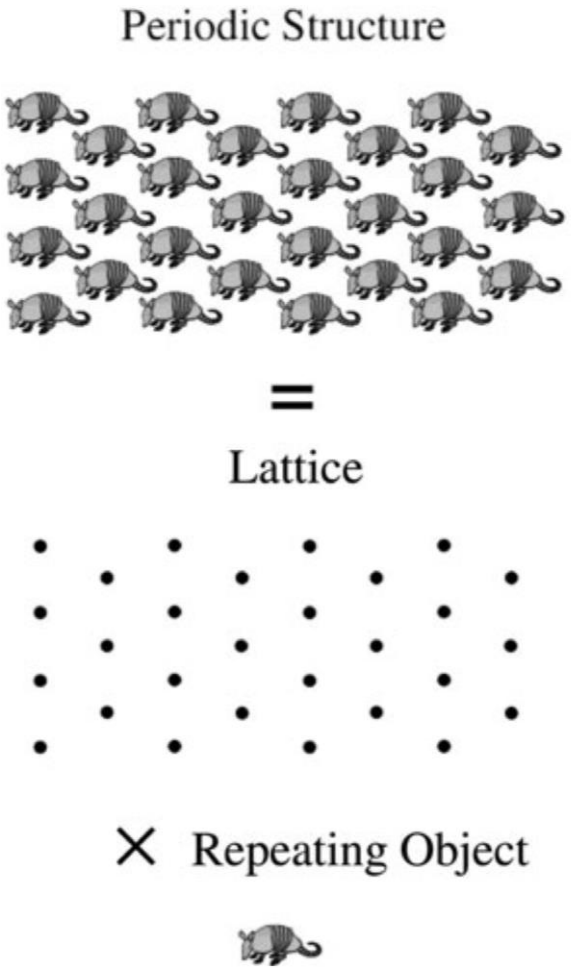
18th Symposium on Experimental Algorithms
June 16-18, 2020
Catania, Italy

diamond · Hartree Centre · Imperial College London · ICNS · King Abdullah University of Science and Technology · University of Southampton

Ionic crystals

Crystal = ***an ordered arrangement of ions, atoms or molecules***

- The crystal structure is periodic.
- Crystal lattice extends in all 3 dimensions.
- The unit cell is a small box containing one or more atoms in a specific spatial arrangement that form the crystal when stacked.



Ionic crystals

Crystal = ***composition*** + *unit cell parameters* + *arrangement of atoms*

Composition

- Chemical formula
  - Element e_i has charge q_i
  - Proportions of ions
- Charge neutral
- Atomic radius ρ_i

Ionic crystals

Crystal = ***composition*** + *unit cell parameters* + *arrangement of atoms*

Composition

- Chemical formula
  - Element e_i has charge q_i
  - Proportions of ions
- Charge neutral
- Atomic radius ρ_i

$SrTiO_3$

Ionic crystals

Crystal = *composition* + ***unit cell parameters*** + *arrangement of atoms*

Unit cell parameters

- Lengths y_1, y_2, y_3
- Angles $\theta_{12}, \theta_{13}, \theta_{23}$

Ionic crystals

Crystal = *composition* + *unit cell parameters* + ***arrangement of atoms***

Arrangement of atoms

- Point $x_i = (x_{i1}, x_{i2}, x_{i3})$ in the unit cell for every ion i
- $d(x_i, x_j)$: distance between x_i and x_j
- $d(x_i, x_j) \geq \rho_i + \rho_j$

Ionic crystals

Crystal = *composition* + *unit cell parameters* + *arrangement of atoms*

Example

- Orthogonal unit cell
  - $\theta_{12} = \theta_{13} = \theta_{23} = 90^o$
- Point $x_i = (x_{i1}, x_{i2}, x_{i3})$ has "copies" in $(k_1 y_1 + x_{i1},\ k_2 y_2 + x_{i2},\ k_3 y_3 + x_{i3})$ for every possible combination of integers k_1, k_2, k_3

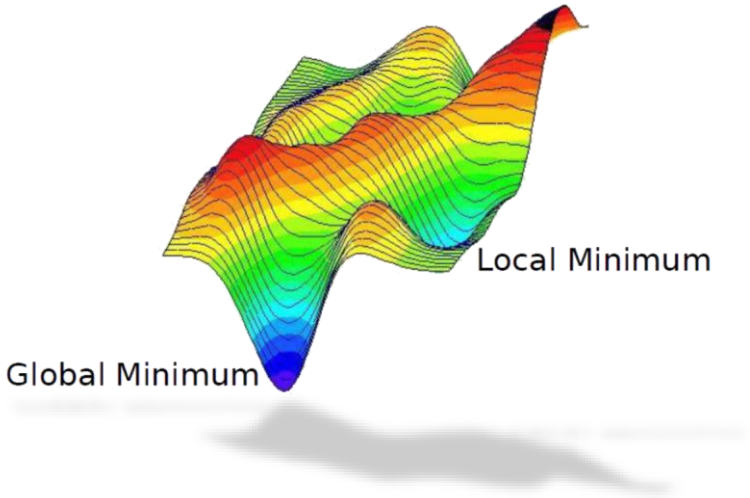
Energy of crystal structures

Energy

- Every combination of unit cell parameters and arrangement of atoms corresponds to an energy.
- Potential Energy Surface
  - 6 unit cell parameters
  - n atoms in the unit cell
  - $3(n-1)+6$ degrees of freedom

Methods for calculating the energy

- Density functional theory (DFT)
  - Accurate, but computationally expensive
- Interatomic forcefields
  - Less accurate, but computationally cheaper

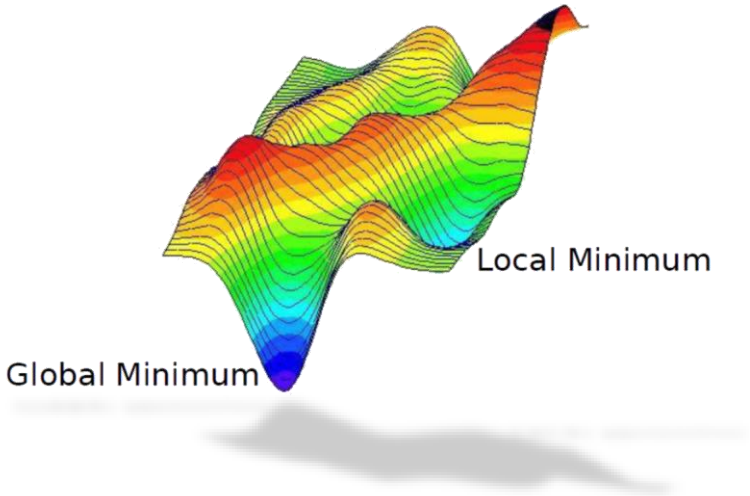


Energy

- Every combination of unit cell parameters and arrangement of atoms corresponds to an energy.
- Potential Energy Surface
  - 6 unit cell parameters
  - n atoms in the unit cell
  - $3(n-1)+6$ degrees of freedom

Methods for calculating the energy

- Density functional theory (DFT)
  - Accurate, but computationally expensive
- Interatomic forcefields
  - Less accurate, but computationally cheaper



Buckingham-Coulomb potential

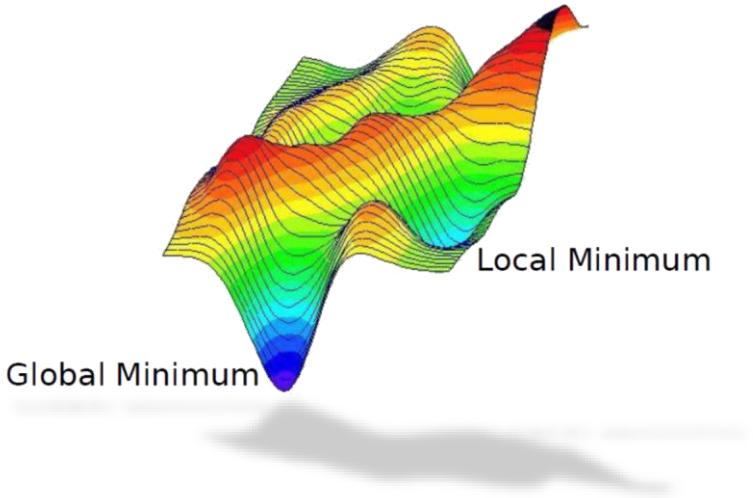
Buckingham – Coulomb potential

Buckingham

- Short range
- Depends on composition-dependent parameters
  - For each pair of elements e_i, e_j we have $A_{e_i e_j}$, $B_{e_i e_j}$ and $C_{e_i e_j}$
- $BE_{i,j} = A_{e_i e_j} \exp\left(-B_{e_i e_j} d(x_i, x_j)\right) - \frac{C_{e_i e_j}}{d(x_i, x_j)^6}$

Coulomb

- Long range
- $CE_{i,j} = \frac{q_i q_j}{d(x_i, x_j)}$



Buckingham – Coulomb potential

Buckingham

- Short range
- Depends on composition-dependent parameters
  - For each pair of elements e_i, e_j we have $A_{e_i e_j}$, $B_{e_i e_j}$ and $C_{e_i e_j}$
- $BE_{i,j} = A_{e_i e_j} \exp\left(-B_{e_i e_j} d(x_i, x_j)\right) - \frac{C_{e_i e_j}}{d(x_i, x_j)^6}$

Coulomb

- Long range
- $CE_{i,j} = \frac{q_i q_j}{d(x_i, x_j)}$

$$E(y, \theta, x) = \lim_{\rho \to \infty} \sum_{i=1}^{n} \sum_{j \neq i, j \in S(x_i, \rho)} (BE_{i,j} + CE_{i,j})$$

Buckingham – Coulomb potential

Buckingham

- Short range
- Depends on composition-dependent parameters
  - For each pair of elements e_i, e_j we have $A_{e_i e_j}$, $B_{e_i e_j}$ and $C_{e_i e_j}$
- $BE_{i,j} = A_{e_i e_j} \exp\left(-B_{e_i e_j} d(x_i, x_j)\right) - \frac{C_{e_i e_j}}{d(x_i, x_j)^6}$

Coulomb

- Long range
- $CE_{i,j} = \frac{q_i q_j}{d(x_i, x_j)}$

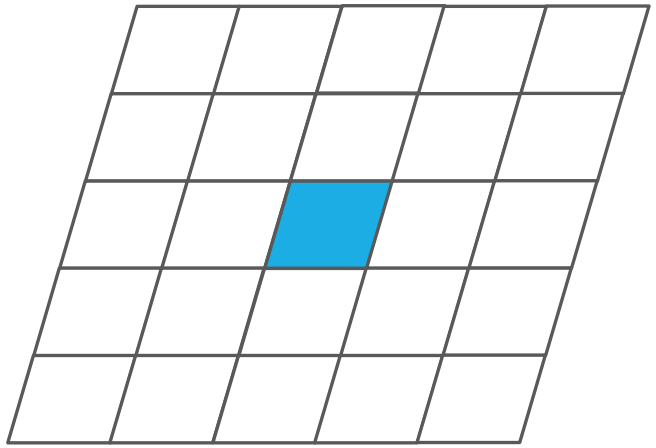
$$E(y, \theta, x) = \lim_{\rho \to \infty} \sum_{i=1}^{n} \sum_{j \neq i, j \in S(x_i, \rho)} (BE_{i,j} + CE_{i,j})$$

Sphere with centre x_i and radius ρ

Energy calculation – A simpler approach

Question 1

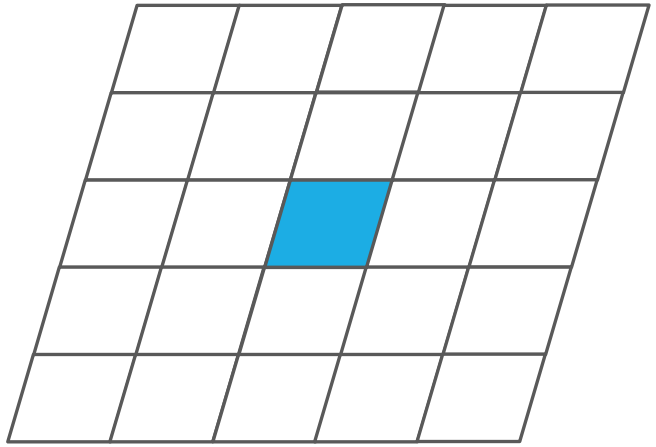
- Given a composition and Buckingham parameters for it, find a simple, combinatorial method to approximate the energy of a crystal structure



Energy calculation – A simpler approach

Question 1

- Given a composition and Buckingham parameters for it, find a simple, combinatorial method to approximate the energy of a crystal structure



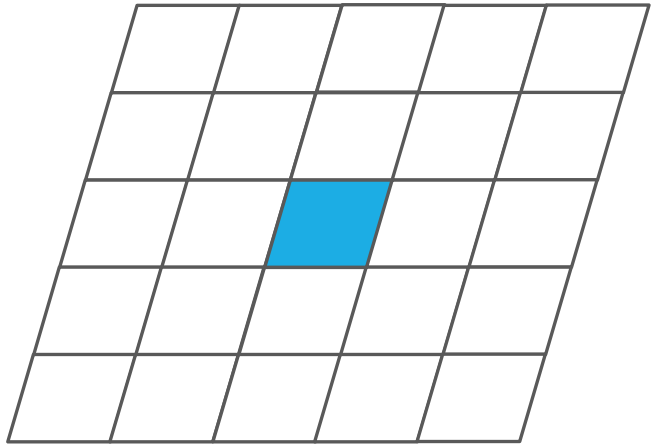
Depth Approach

- Given a parameter k, it creates k layers around the unit cell with copies of the structure.
- $$E(y,\theta,x) = \lim_{\rho\to\infty} \sum_{i=1}^{n} \sum_{j\neq i, j\in S(x_i,\rho)} (BE_{i,j} + CE_{i,j})$$

Energy calculation – A simpler approach

Question 1

- Given a composition and Buckingham parameters for it, find a simple, combinatorial method to approximate the energy of a crystal structure



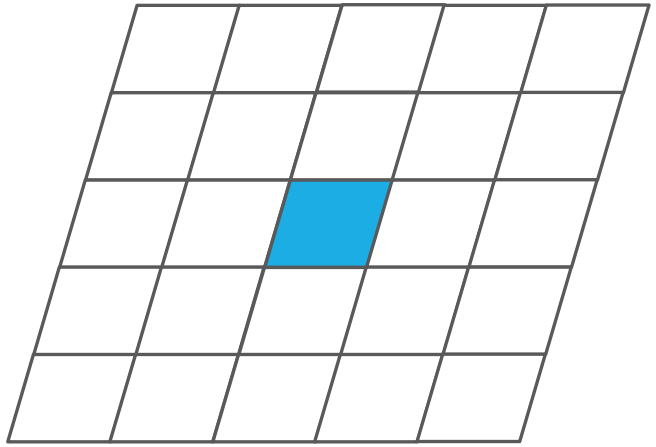
Depth Approach

- Given a parameter k, it creates k layers around the unit cell with copies of the structure.
- $$E(y,\theta,x) = \lim_{\rho\to\infty} \sum_{i=1}^{n} \sum_{j \neq i, j \in S(x_i,\rho)} (BE_{i,j} + CE_{i,j})$$

Energy calculation – A simpler approach

Question 1

- Given a composition and Buckingham parameters for it, find a simple, combinatorial method to approximate the energy of a crystal structure



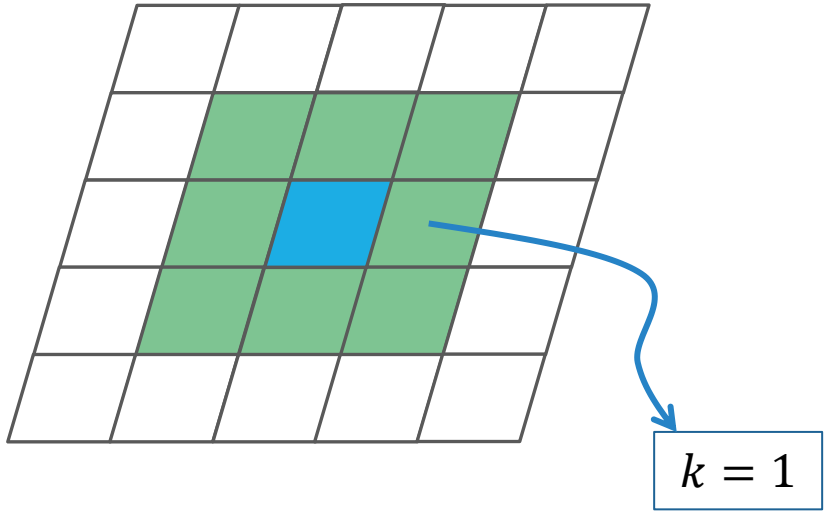
Depth Approach

- Given a parameter k, it creates k layers around the unit cell with copies of the structure.
- $$E(y,\theta,x) = \lim_{\rho\to\infty} \sum_{i=1}^{n} \sum_{j\neq i, j\in D(k)} (BE_{i,j} + CE_{i,j})$$

Energy calculation – A simpler approach

Question 1

- Given a composition and Buckingham parameters for it, find a simple, combinatorial method to approximate the energy of a crystal structure



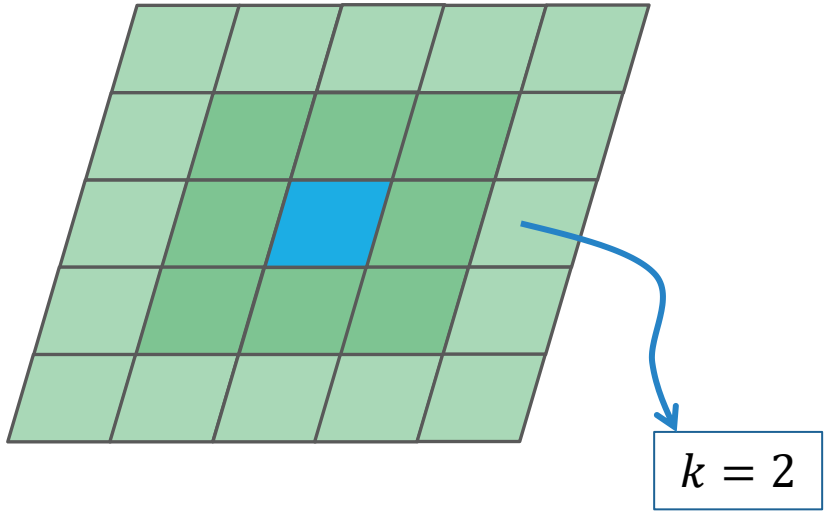
Depth Approach

- Given a parameter k, it creates k layers around the unit cell with copies of the structure.
- $$E(y, \theta, x) = \lim_{\rho \to \infty} \sum_{i=1}^{n} \sum_{j \neq i, j \in D(k)} (BE_{i,j} + CE_{i,j})$$

Energy calculation – A simpler approach

Question 1

- Given a composition and Buckingham parameters for it, find a simple, combinatorial method to approximate the energy of a crystal structure



Depth Approach

- Given a parameter k, it creates k layers around the unit cell with copies of the structure.
- $$E(y, \theta, x) = \lim_{\rho \to \infty} \sum_{i=1}^{n} \sum_{j \neq i, j \in D(k)} (BE_{i,j} + CE_{i,j})$$

Energy calculation – A simpler approach

Experimental results

- Comparison between depth approach and GULP for $\mathrm{SrTiO_3}$.

Depth Approach

- Given a parameter k, it creates k layers around the unit cell with copies of the structure.
- $$E(y,\theta,x) = \lim_{\rho\to\infty} \sum_{i=1}^{n} \sum_{j\neq i, j\in D(k)} (BE_{i,j} + CE_{i,j})$$

Energy calculation – A simpler approach

Experimental results

- Comparison between depth approach and GULP for $SrTiO_3$.
- Fast convergence

Depth Approach

- Given a parameter k, it creates k layers around the unit cell with copies of the structure.
- $$E(y,\theta,x) = \lim_{\rho\to\infty} \sum_{i=1}^{n} \sum_{j\neq i, j\in D(k)} (BE_{i,j} + CE_{i,j})$$

	Energy difference					
k	1	2	3	4	5	6
15 atoms	0.0639	0.0226	0.0114	0.0068	0.0045	0.0032
20 atoms	0.0670	0.0238	0.0120	0.0072	0.0047	0.0033

Energy calculation – A simpler approach

Experimental results

- Comparison between depth approach and GULP for $\mathrm{SrTiO_3}$.
- Fast convergence
- "Monotonicity"
  - **For any $k \geq 1$, the relative energies between any two *feasible* arrangements remain almost always the same.**

Depth Approach

- Given a parameter k, it creates k layers around the unit cell with copies of the structure.
- $$E(y, \theta, x) = \lim_{\rho \to \infty} \sum_{i=1}^{n} \sum_{j \neq i, j \in D(k)} (BE_{i,j} + CE_{i,j})$$

Energy calculation – A simpler approach

Experimental results

- Comparison between depth approach and GULP for $SrTiO_3$.
- Fast convergence
- "Monotonicity"
  - **For any $k \geq 1$, the relative energies between any two *feasible* arrangements remain almost always the same.**

Depth Approach

- Given a parameter k, it creates k layers around the unit cell with copies of the structure.
- $$E(y, \theta, x) = \lim_{\rho \to \infty} \sum_{i=1}^{n} \sum_{j \neq i, j \in D(k)} (BE_{i,j} + CE_{i,j})$$

$E_1(x)$: energy of arrangement x for $k = 1$.
$E_G(x)$: energy of arrangement x computed by GULP.

✓ If for two random (feasible) configurations x_i and x_j it holds that $E_1(x_i) < E_1(x_j)$, then $E_G(x_i) < E_G(x_j)$ for almost all pairs x_i and x_j.

Energy calculation – A simpler approach

Experimental results

- Comparison between depth approach and GULP for $SrTiO_3$.
- Fast convergence
- "Monotonicity"
  - **For any $k \geq 1$, the relative energies between any two *feasible* arrangements remain almost always the same.**

Depth Approach

- Given a parameter k, it creates k layers around the unit cell with copies of the structure.
- $$E(y, \theta, x) = \lim_{\rho \to \infty} \sum_{i=1}^{n} \sum_{j \neq i, j \in D(k)} (BE_{i,j} + CE_{i,j})$$

Formal proof?

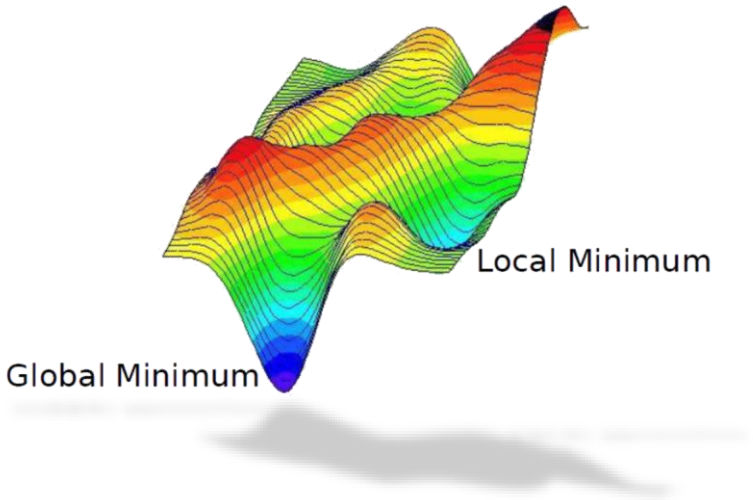
$E_1(x)$: energy of arrangement x for $k = 1$.
$E_G(x)$: energy of arrangement x computed by GULP.

✓ If for two random (feasible) configurations x_i and x_j it holds that $E_1(x_i) < E_1(x_j)$, then $E_G(x_i) < E_G(x_j)$ for almost all pairs x_i and x_j.

Crystal Structure Prediction

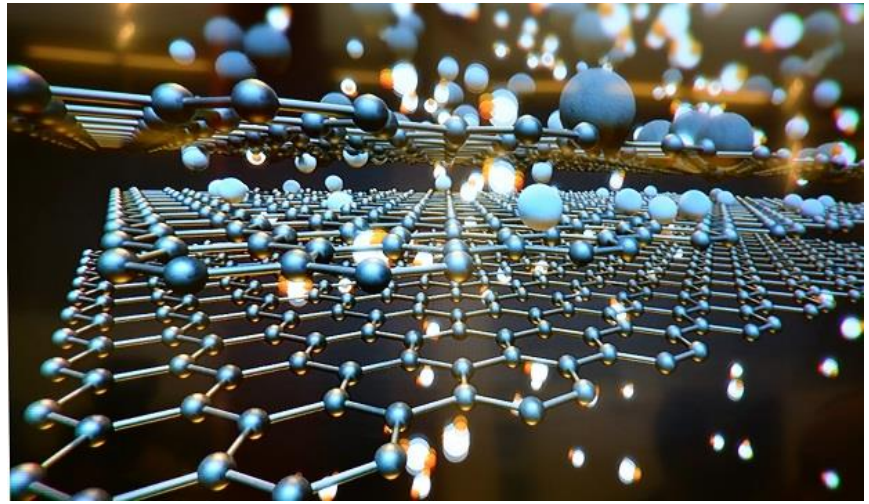
Crystal Structure Prediction

- Crystal structure prediction (CSP) is the calculation of the crystal structures of solids.
- The most stable structure corresponds to the global minimum of the potential energy surface.
- Computational methods employed include:
  - genetic/evolutionary algorithms
  - basin hopping
  - simulated annealing
  - data mining, etc.

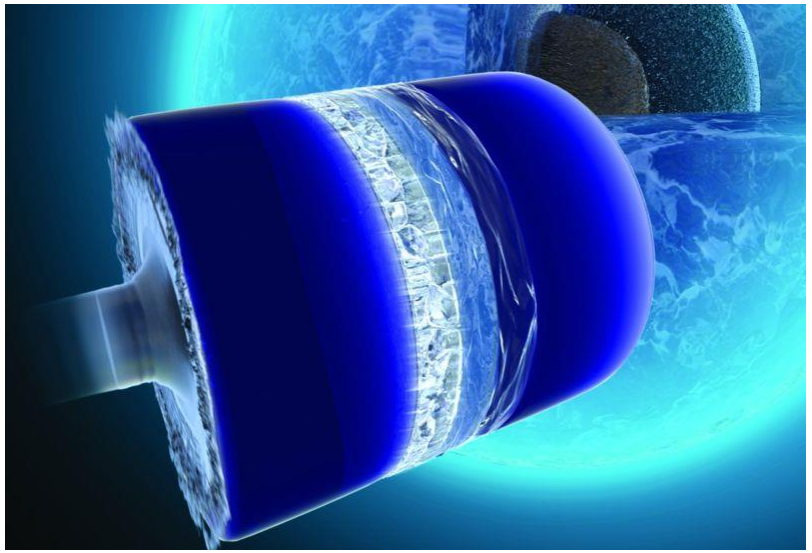


Crystal Structure Prediction - Applications

- Move from *ad-hoc Edisonian* approach to a systematic theoretical approach
  - Search for materials purely on computer by the aimed properties, and then guide the experimentalist to synthesize them in the laboratory
- Search for materials with desired properties
  - make safer, lighter vehicles
  - better food packaging
  - cheap solar cells, etc.



Crystal Structure Prediction - Applications



Nanosecond freezing of water at high pressures: nucleation and growth near the metastability limit, Philip C. Myint et al.

- Obtain structural information of materials under any external conditions
  - high pressure
  - variable temperature
  - high radiation fluxes
  - strong electric/magnetic field

Crystal Structure Prediction - Questions

Question 1 - MinEnergy

- Input: A composition with its corresponding Buckingham constants, a positive n, and a rational $\hat{E}$.
- Question: Is there a crystal structure (y, θ, x) for the composition with n ions that is neutrally charged and achieves Buckingham-Coulomb energy $E(y, \theta, x) < \hat{E}$?

Question 2 - MinStructure

- Input: A composition with its corresponding Buckingham constants and a positive n.
- Task: Find a crystal structure (y, θ, x) for the composition with n ions that is neutrally charged and the Buckingham-Coulomb energy $E(y, \theta, x)$ is minimized.

Crystal Structure Prediction - Questions

Question 3 - AvgEnergy

- Input: A composition with its corresponding Buckingham constants and a rational $\hat{E}$.
- Question: Is there a crystal structure for the composition that is neutrally charged and $\frac{E(y,\theta,x)}{n} < \hat{E}$?

Question 4 - AvgStructure

- Input: A composition with its corresponding Buckingham constants.
- Task: Find a crystal structure for the composition that is neutrally charged and the average Buckingham-Coulomb energy per ion in the unit cell, $\frac{E(y,\theta,x)}{n}$, is minimized.

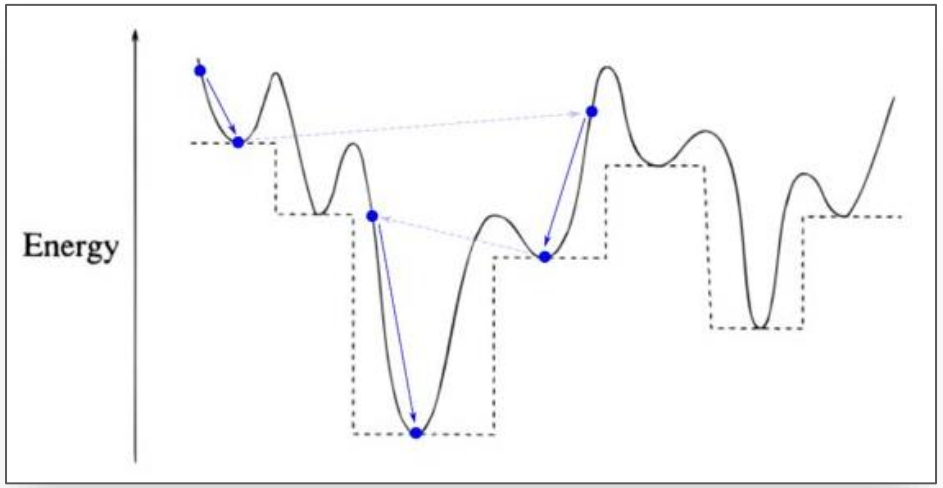
Unbounded number of atoms

The general method for MinStructure

Given a current solution x, choose a new potential solution x'.

Perform gradient descent on the potential energy surface starting from x'.
This is known as relaxation.

Decide whether to keep x as the current solution, or to update it to the solution found after relaxing x'.



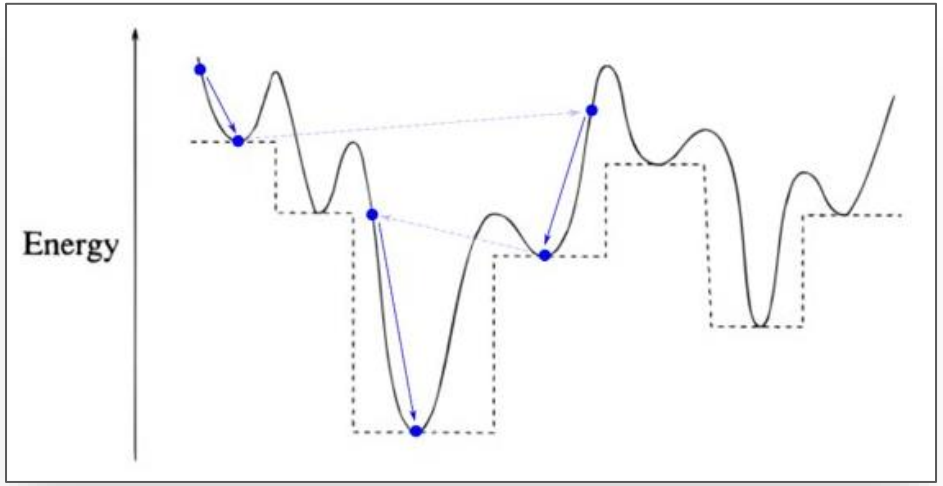
The general method for MinStructure

Given a current solution x, choose a new potential solution x'.

Perform gradient descent on the potential energy surface starting from x'.
This is known as relaxation.

Decide whether to keep x as the current solution, or to update it to the solution found after relaxing x'.

- Genetic algorithms
- Simulated annealing
- Basin hopping



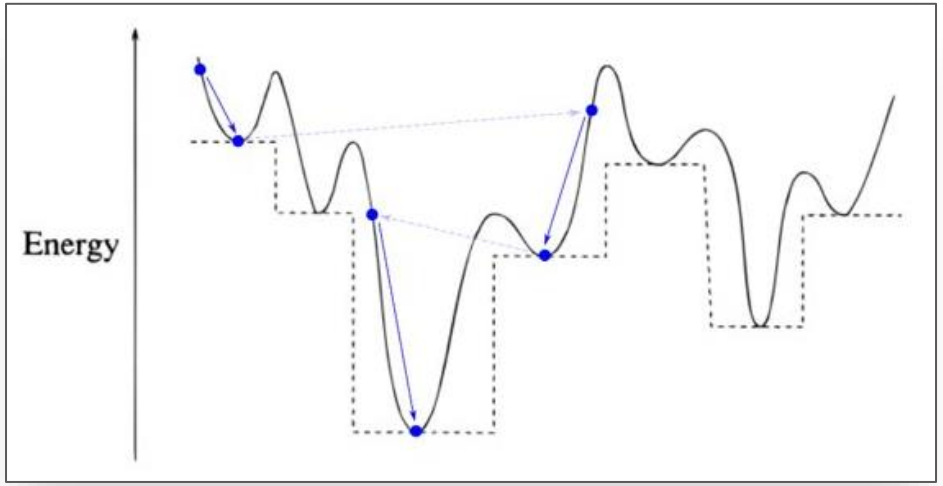
The general method for MinStructure

Given a current solution x, choose a new potential solution x'.

Perform gradient descent on the potential energy surface starting from x'.
This is known as relaxation.

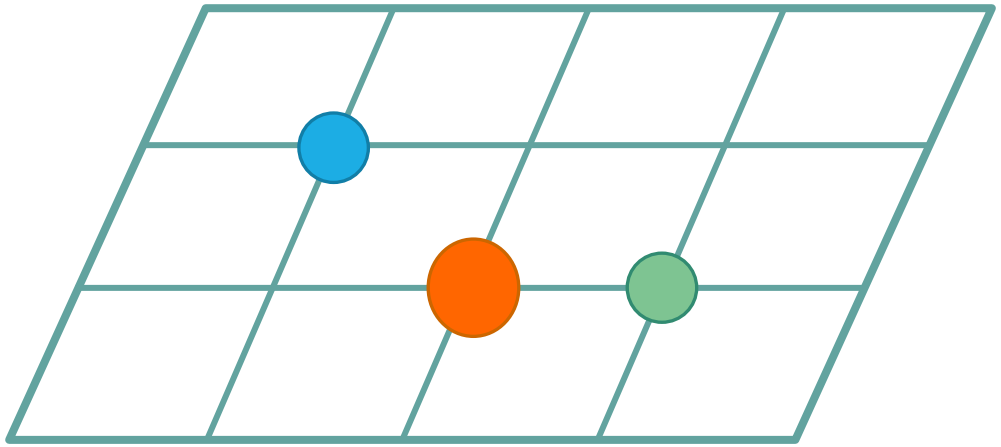
Decide whether to keep x as the current solution, or to update it to the solution found after relaxing x'.

- Genetic algorithms
- Simulated annealing
- Basin hopping and Local Search



Oblivious Local Search

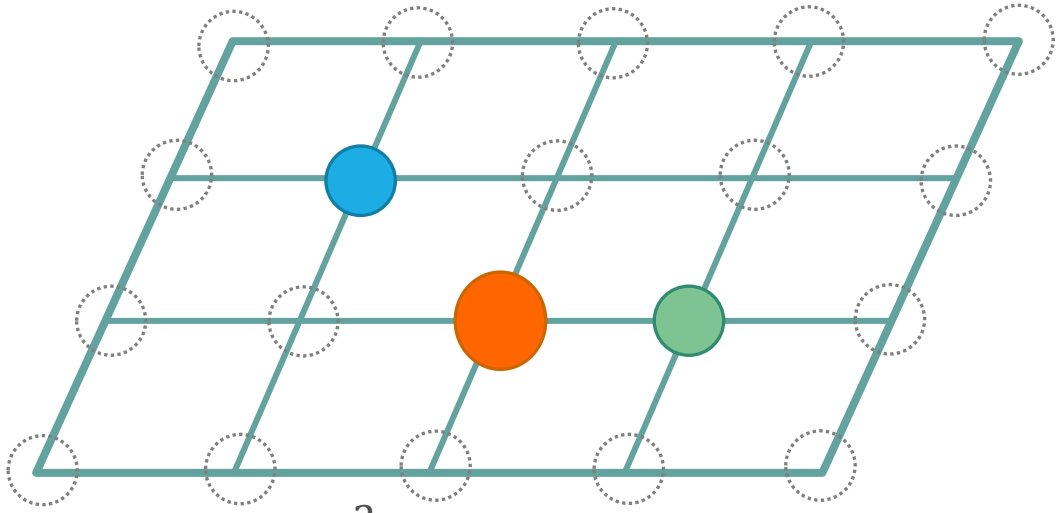
- Discretize unit cell
- Ions are placed on the nodes of the grid
- Local search neighbourhoods
  - k-ion swap
  - k swap
  - Axes



2-ion swap

Oblivious Local Search

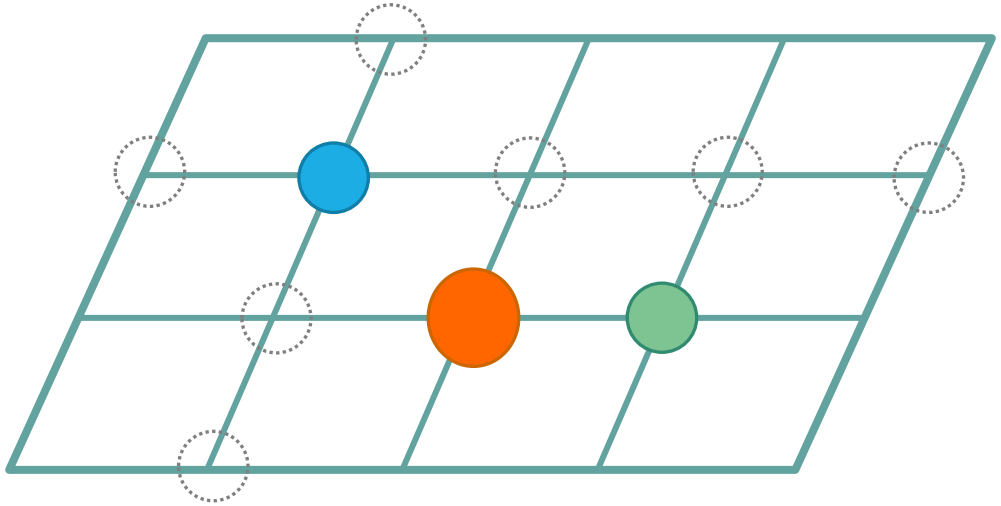
- Discretize unit cell
- Ions are placed on the nodes of the grid
- Local search neighbourhoods
  - k-ion swap
  - k swap
  - Axes



2 swap

Oblivious Local Search

- Discretize unit cell
- Ions are placed on the nodes of the grid
- Local search neighbourhoods
  - k-ion swap
  - k swap
  - Axes



Oblivious Local Search

Neighbourhood	Running time	Time stdev	Energy drop	Energy drop stdev
Axes	5.36	1.54	13.46	10.60
2-ion swap	0.96	0.33	7.75	8.45
2-swap	34.66	14.06	16.21	10.94

Neighbourhood	Running time	Time stdev	Energy drop	Energy drop stdev	Global minimum
Random structures-GULP	8.80	6.35	18.60	10.26	6.6%
Axes-GULP	7.92	6.16	5.53	2.28	10.0%
2-ion swap-GULP	8.82	6.25	11.09	5.64	4.7%
2-swap-GULP	5.14	5.08	2.79	1.05	14.8%

$SrTiO_3$ with 15 atoms per unit cell and discretization parameter $\delta = 1$Å (375 grid points). Energy is in electronvolts (eV). Results averaged over 1000 initial configurations.

Oblivious Local Search

Neighbourhood	Running time	Time stdev	Energy drop	Energy drop stdev
Axes	5.36	1.54	13.46	10.60
2-ion swap	0.96	0.33	7.75	8.45
2-swap	34.66	14.06	16.21	10.94

Neighbourhood	Running time	Time stdev	Energy drop	Energy drop stdev	Global minimum
Random structures-GULP	8.80	6.35	18.60	10.26	6.6%
Axes-GULP	7.92	6.16	5.53	2.28	10.0%
2-ion swap-GULP	8.82	6.25	11.09	5.64	4.7%
2-swap-GULP	5.14	5.08	2.79	1.05	14.8%

$SrTiO_3$ with 15 atoms per unit cell and discretization parameter $\delta = 1$Å (375 grid points). Energy is in electronvolts (eV). Results averaged over 1000 initial configurations.

Oblivious Local Search

Neighbourhood	Running time	Time stdev	Energy drop	Energy drop stdev
Axes	5.36	1.54	13.46	10.60
2-ion swap	0.96	0.33	7.75	8.45
2-swap	34.66	14.06	16.21	10.94

Neighbourhood	Running time	Time stdev	Energy drop	Energy drop stdev	Global minimum
Random structures-GULP	8.80	6.35	18.60	10.26	6.6%
Axes-GULP	7.92	6.16	5.53	2.28	10.0%
2-ion swap-GULP	8.82	6.25	11.09	5.64	4.7%
2-swap-GULP	5.14	5.08	2.79	1.05	14.8%

$SrTiO_3$ with 15 atoms per unit cell and discretization parameter $\delta = 1$Å (375 grid points). Energy is in electronvolts (eV). Results averaged over 1000 initial configurations.

Oblivious Local Search

Neighbourhood	Running time	Time stdev	Energy drop	Energy drop stdev
Axes	5.36	1.54	13.46	10.60
2-ion swap	0.96	0.33	7.75	8.45
2-swap	34.66	14.06	16.21	10.94

Neighbourhood	Running time	Time stdev	Energy drop	Energy drop stdev	Global minimum
Random structures-GULP	8.80	6.35	18.60	10.26	6.6%
Axes-GULP	7.92	6.16	5.53	2.28	10.0%
2-ion swap-GULP	8.82	6.25	11.09	5.64	4.7%
2-swap-GULP	5.14	5.08	2.79	1.05	14.8%

$SrTiO_3$ with 15 atoms per unit cell and discretization parameter $\delta = 1$Å (375 grid points). Energy is in electronvolts (eV). Results averaged over 1000 initial configurations.

Global optimization

1. Random (feasible) configuration of atoms on the grid.
2. Greedy strategy
   - Among all configurations in the Axes neighbourhood, we choose the one with the minimum energy.
   - Until it cannot further improve the solution.
3. Relaxation (local optimization).

Algorithm	Number of atoms	Total time mean	Total time stdev	Relaxations	Time for relaxations	Time for local search
Axes-GULP	15	227.89	287.21	13.24	126.26	101.63
	20	2280.57	781.66	104.33	1016.72	1049.13
Basin hopping	15	167.89	114.89	18.14	160.79	–
	20	5766.20	4748.33	450.66	4895.60	–

$SrTiO_3$ with 15 and 20 atoms per unit cell and discretization parameter $\delta = 1$Å (375 grid points). Energy is in electronvolts (eV). Results averaged over 200 runs.

Global optimization

1. Random (feasible) configuration of atoms on the grid.
2. Greedy strategy
   - Among all configurations in the Axes neighbourhood, we choose the one with the minimum energy.
   - Until it cannot further improve the solution.
3. Relaxation (local optimization).

Algorithm	Number of atoms	Total time mean	Total time stdev	Relaxations	Time for relaxations	Time for local search
Axes-GULP	15	227.89	287.21	13.24	126.26	101.63
	20	2280.57	781.66	104.33	1016.72	1049.13
Basin hopping	15	167.89	114.89	18.14	160.79	–
	20	5766.20	4748.33	450.66	4895.60	–

$SrTiO_3$ with 15 and 20 atoms per unit cell and discretization parameter $\delta = 1$Å (375 grid points). Energy is in electronvolts (eV). Results averaged over 200 runs.

Global optimization

1. Random (feasible) configuration of atoms on the grid.
2. Greedy strategy
   - Among all configurations in the Axes neighbourhood, we choose the one with the minimum energy.
   - Until it cannot further improve the solution.
3. Relaxation (local optimization).

Algorithm	Number of atoms	Total time mean	Total time stdev	Relaxations	Time for relaxations	Time for local search
Axes-GULP	15	227.89	287.21	13.24	126.26	101.63
	20	2280.57	781.66	104.33	1016.72	1049.13
Basin hopping	15	167.89	114.89	18.14	160.79	–
	20	5766.20	4748.33	450.66	4895.60	–

$SrTiO_3$ with 15 and 20 atoms per unit cell and discretization parameter $\delta = 1$Å (375 grid points). Energy is in electronvolts (eV). Results averaged over 200 runs.

Conclusions and future work

- We introduced and studied Crystal Structure Prediction through the lens of computer science.
- Identified several open questions whose solution would have significant impact to the discovery of new materials.

1. Formal result for our conjecture that the arrangement that minimizes the energy for some small depth k matches the arrangement that minimizes the energy when it is computed by GULP
2. Neighbourhoods that outperform the Axes neighbourhood
3. Can local search improve existing methods for CSP?
4. What happens if we leave the unit cell parameters free?
5. Ultimate goal is to find algorithms for questions 3 and 4

Thank you

Questions?

theofila@liverpool.ac.uk