"Why PES-imism is a Good Thing"

OR

Evolution of the Potential Energy Surface with size for Lennard-Jones Clusters

Jonathan P. K. Doye, Mark A. Miller, and David J. Wales

J. Chem. Phys. **111** 8417-8428 (1999)

Luke Abraham

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http://www-users.york.ac.uk/~nla101

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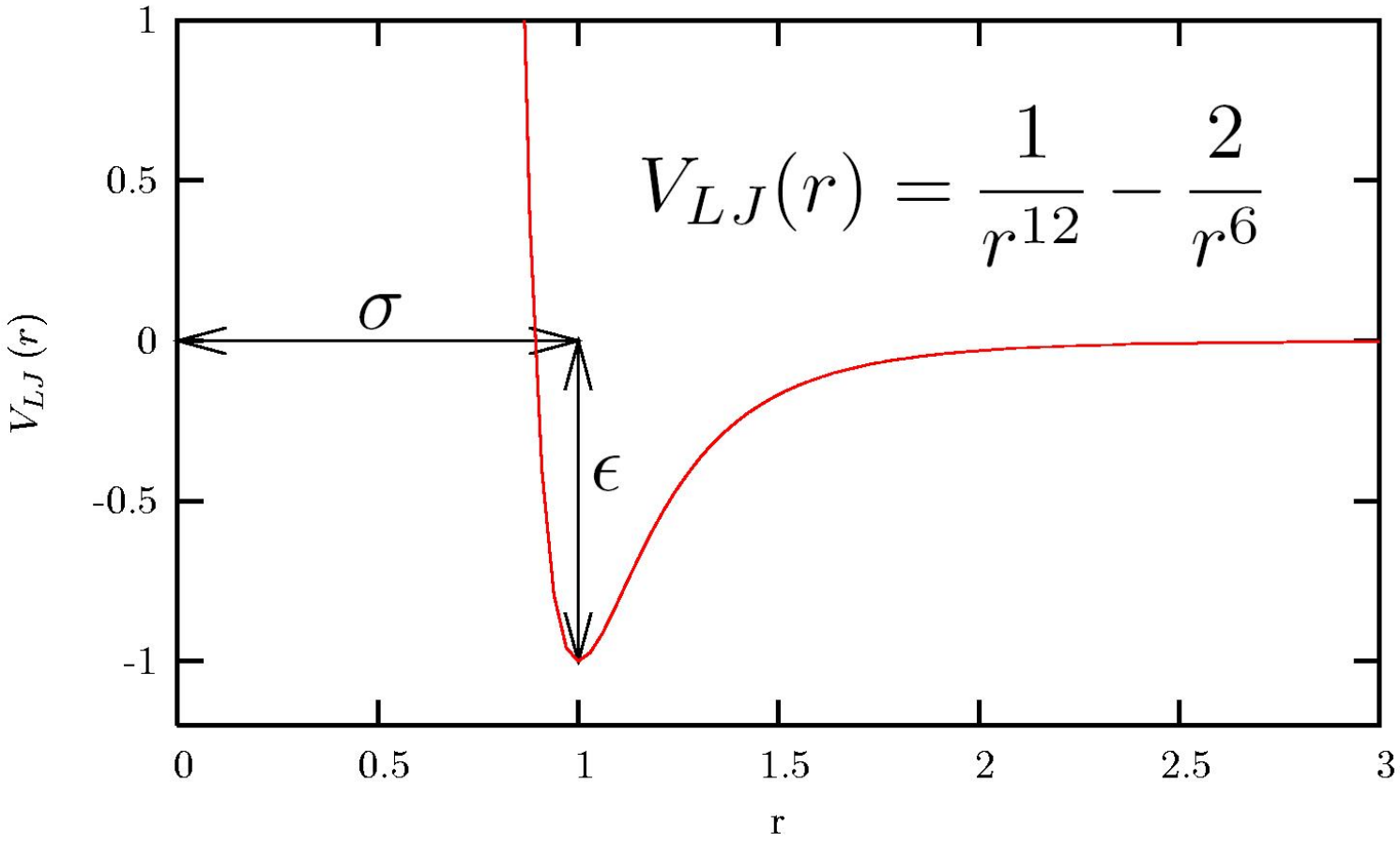
Outline of Talk

- Lennard-Jones clusters.
- Disconnectivity graphs:
  - What are disconnectivity graphs?
  - How can they help visualise the potential energy surface?
- Basin hopping.
- Applications
- My research
- Conclusions

Lennard-Jones Clusters



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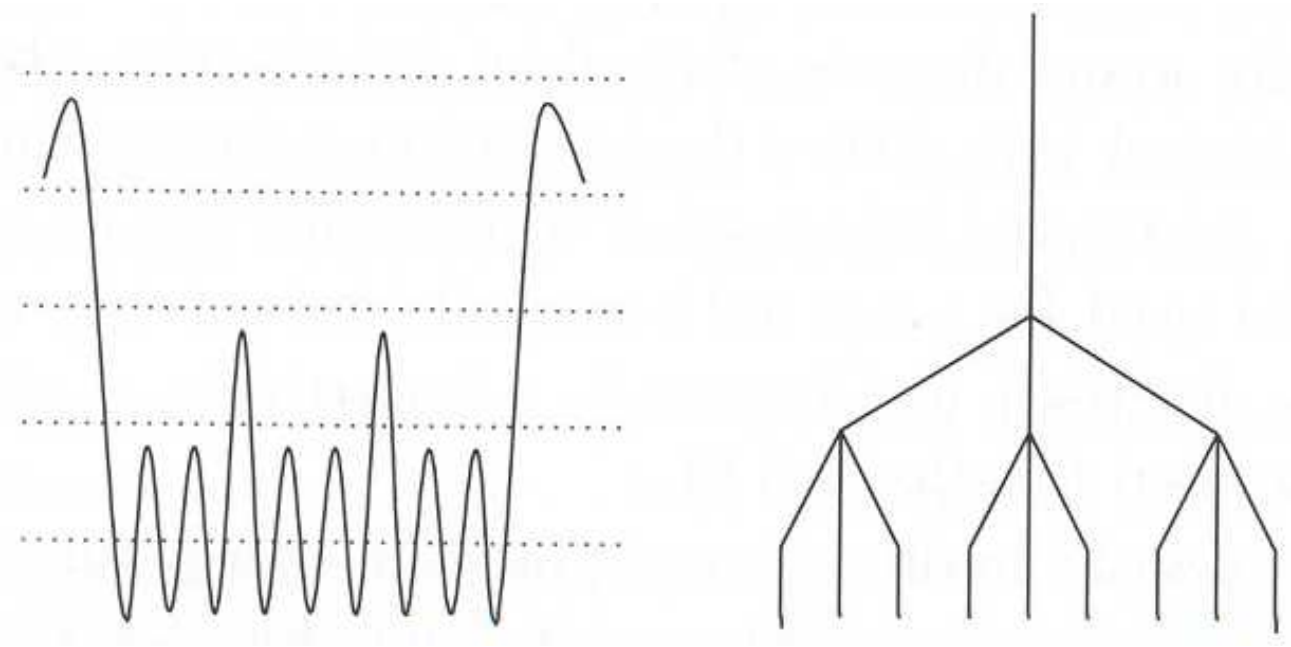
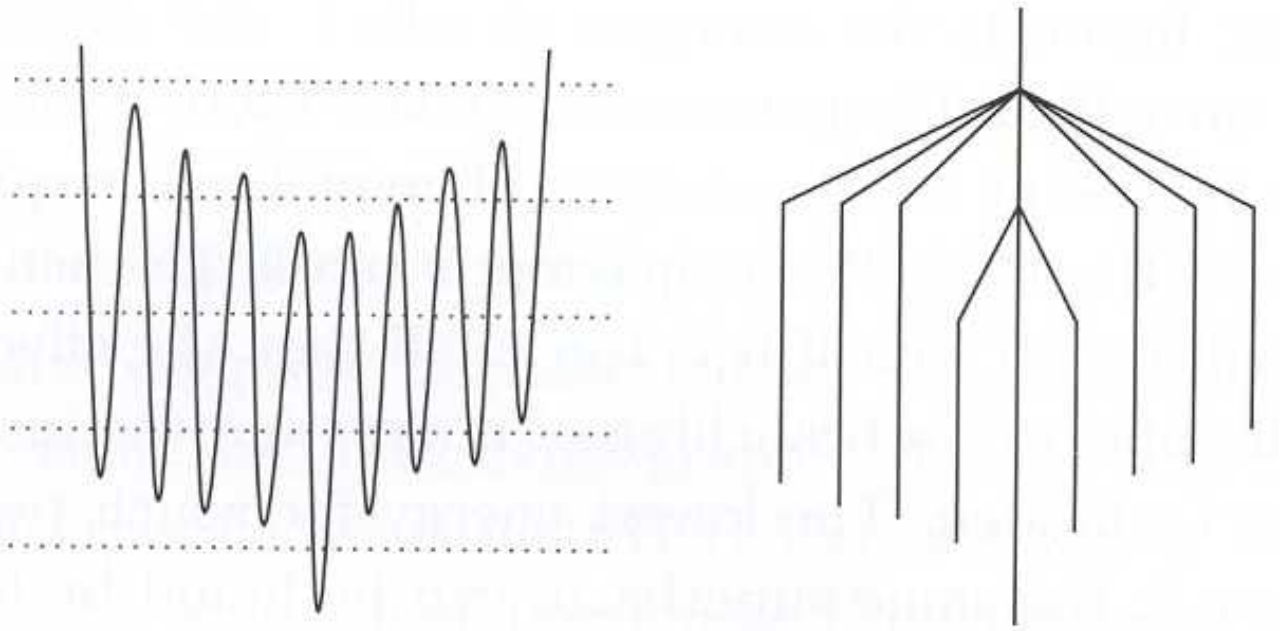
Disconnectivity Graphs

- Potential Energy Surface (PES) - easy to visualise in one or two dimensions
- however - clusters of N atoms have $3N$ dimensional variables
- how can the PES be visualised in a satisfactory way?
- one possible solution - *disconnectivity graphs*

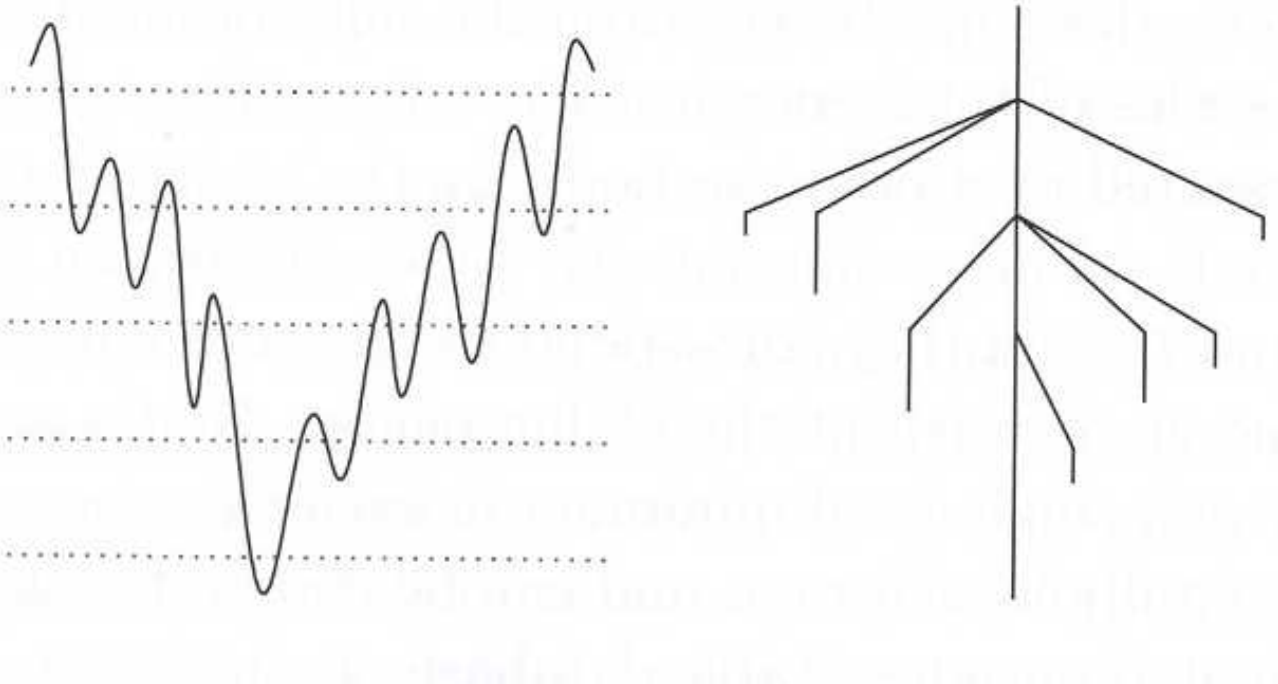
How to form Disconnectivity Graphs



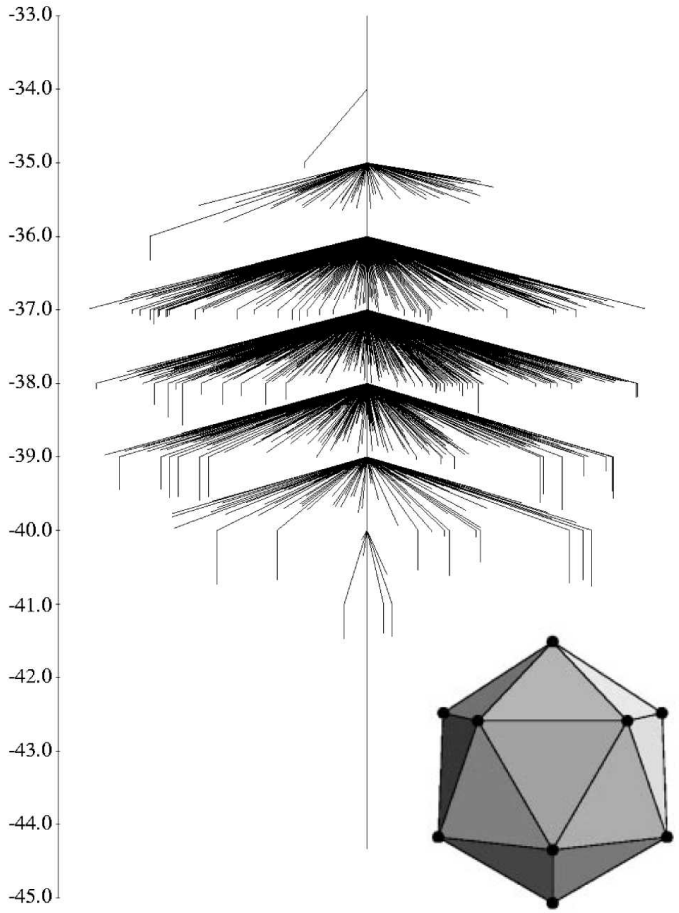
How to form Disconnectivity Graphs



How to form Disconnectivity Graphs



Disconnectivity Graph for the $N = 13$ Cluster



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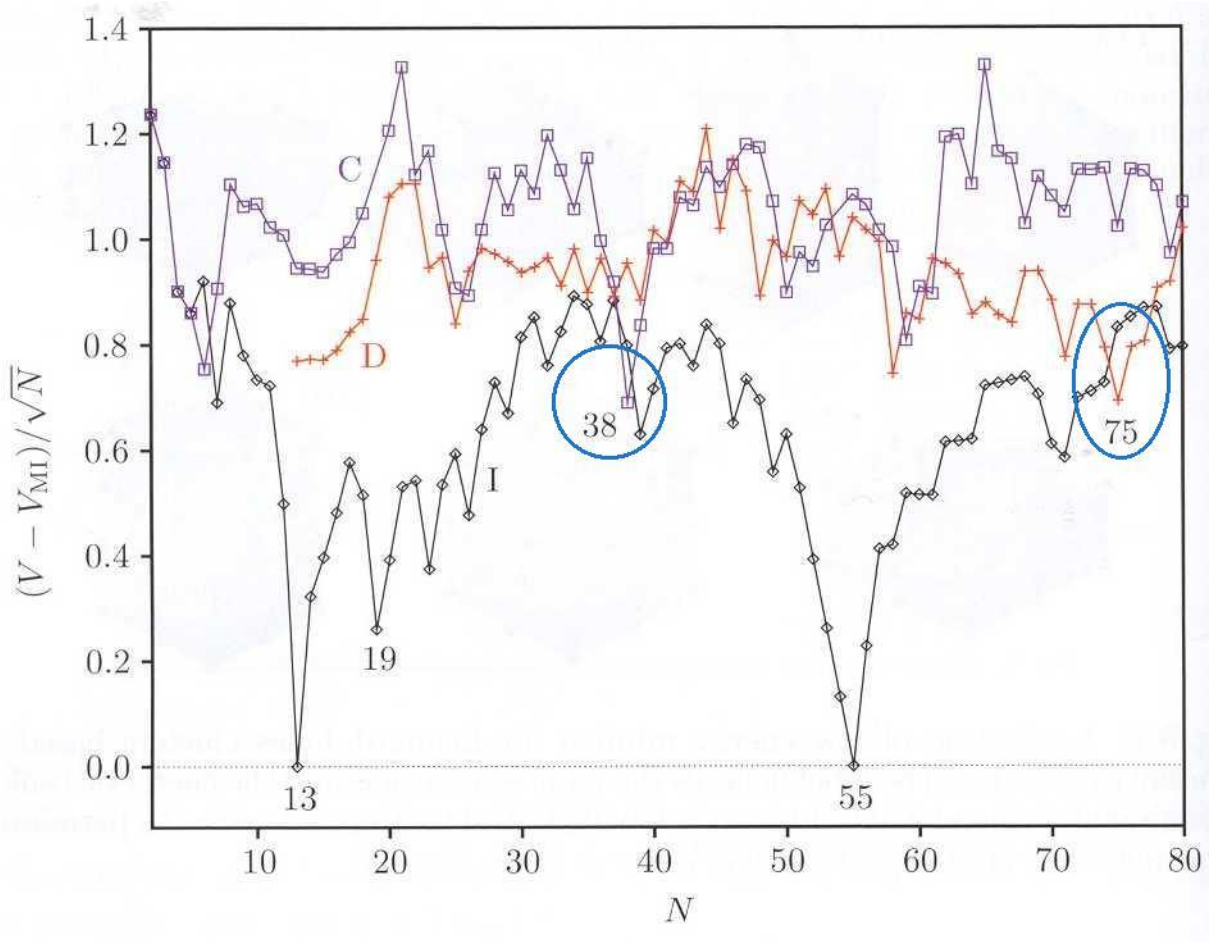
Magic Numbers

- Lennard-Jones clusters usually form around Mackay Icosahedra
  - magic numbers 13, 55, 147, 309,... etc.
- However
  - some clusters do not form around this type of structure
  - smallest N this occurs at is $N = 38$
  - also occurs at e.g. $75 \leq N \leq 77$, $N = 98$ and $102 \leq N \leq 104$

Magic Numbers



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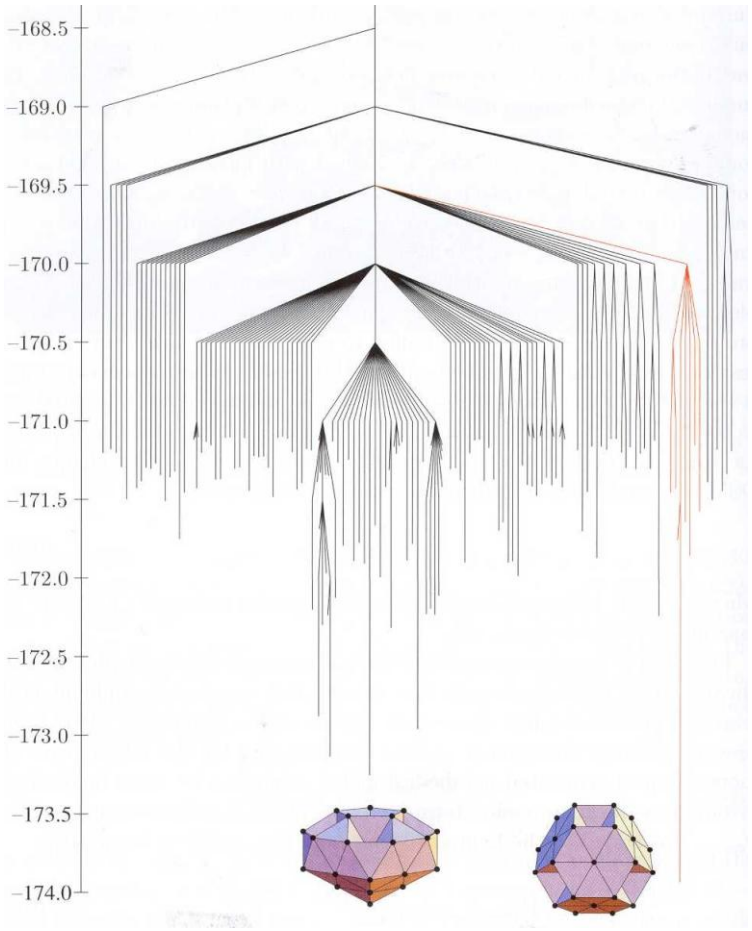
Disconnectivity Graph for the $N = 38$ Cluster



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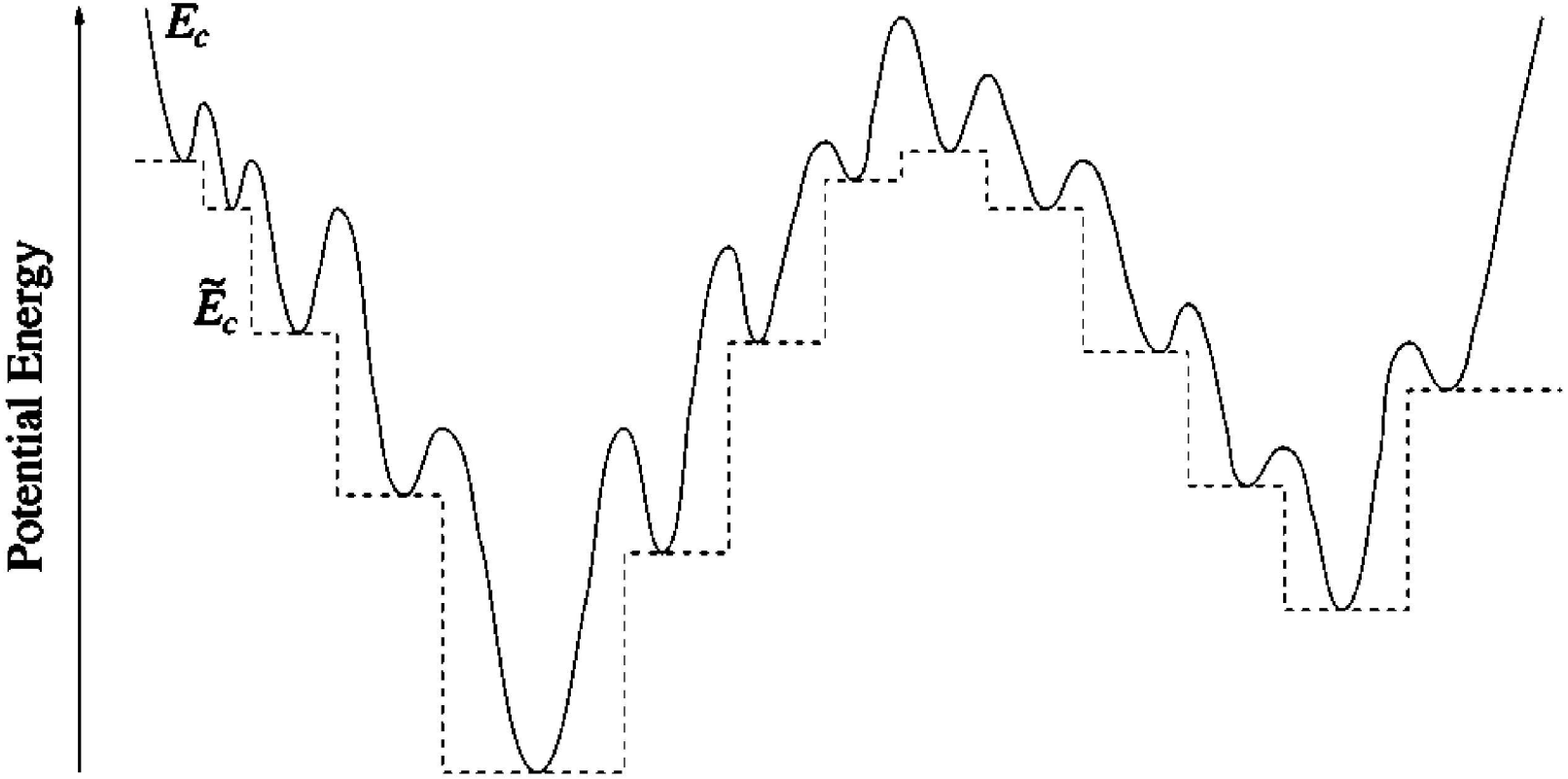
Basin Hopping

- Transformation of the energy surface

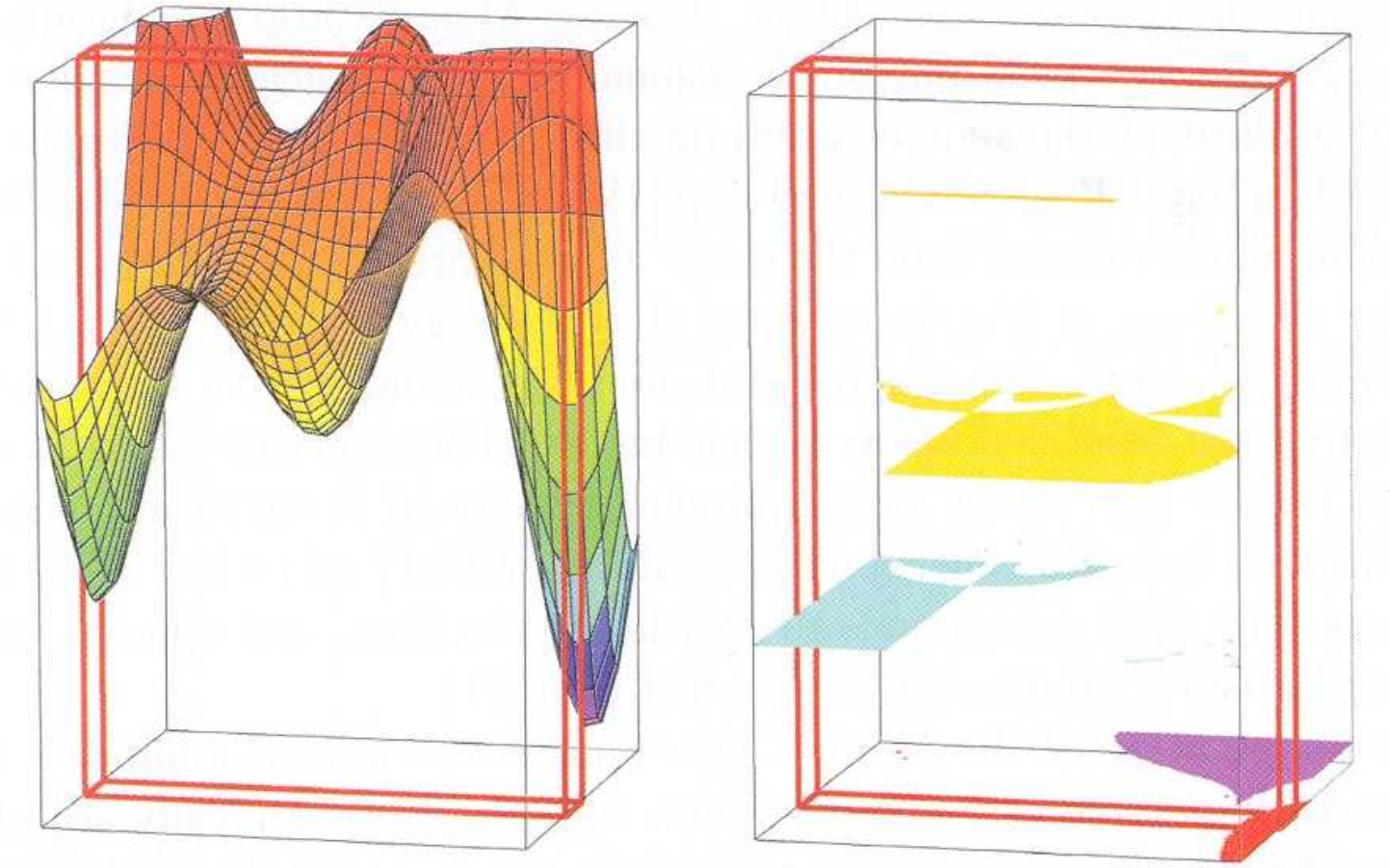
$$\tilde{\mathrm{E}}_c\left(\mathbf{X}\right) = \min\{\mathrm{E}_c\left(\mathbf{X}\right)\} \tag{1}$$

- Monte Carlo search technique
- simplifies PES *but* global minima remains the same

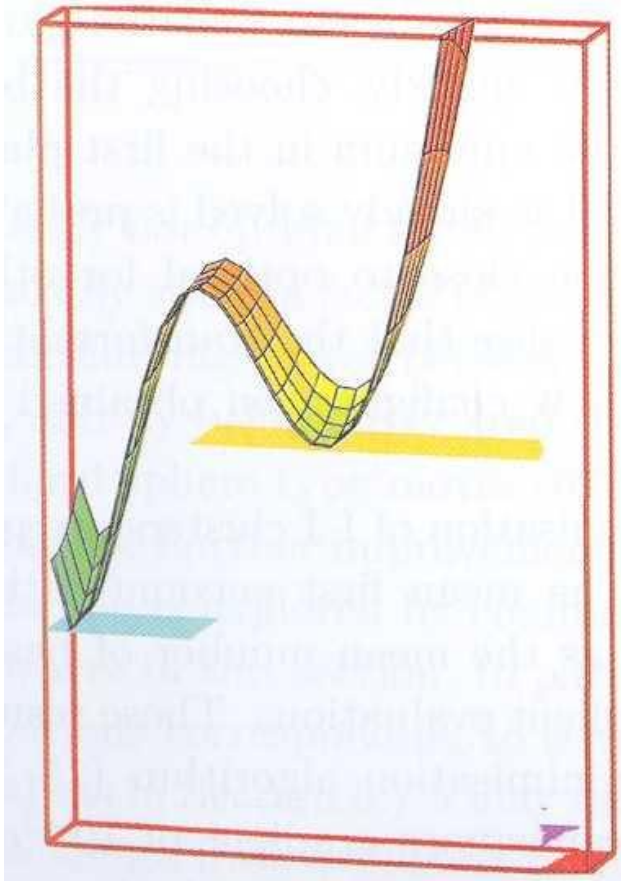
Basin Hopping

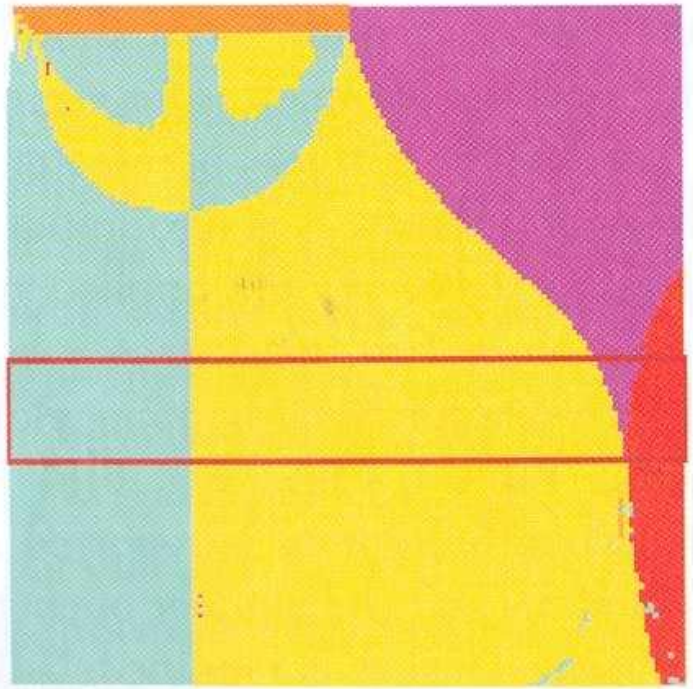


Basin Hopping in 2D

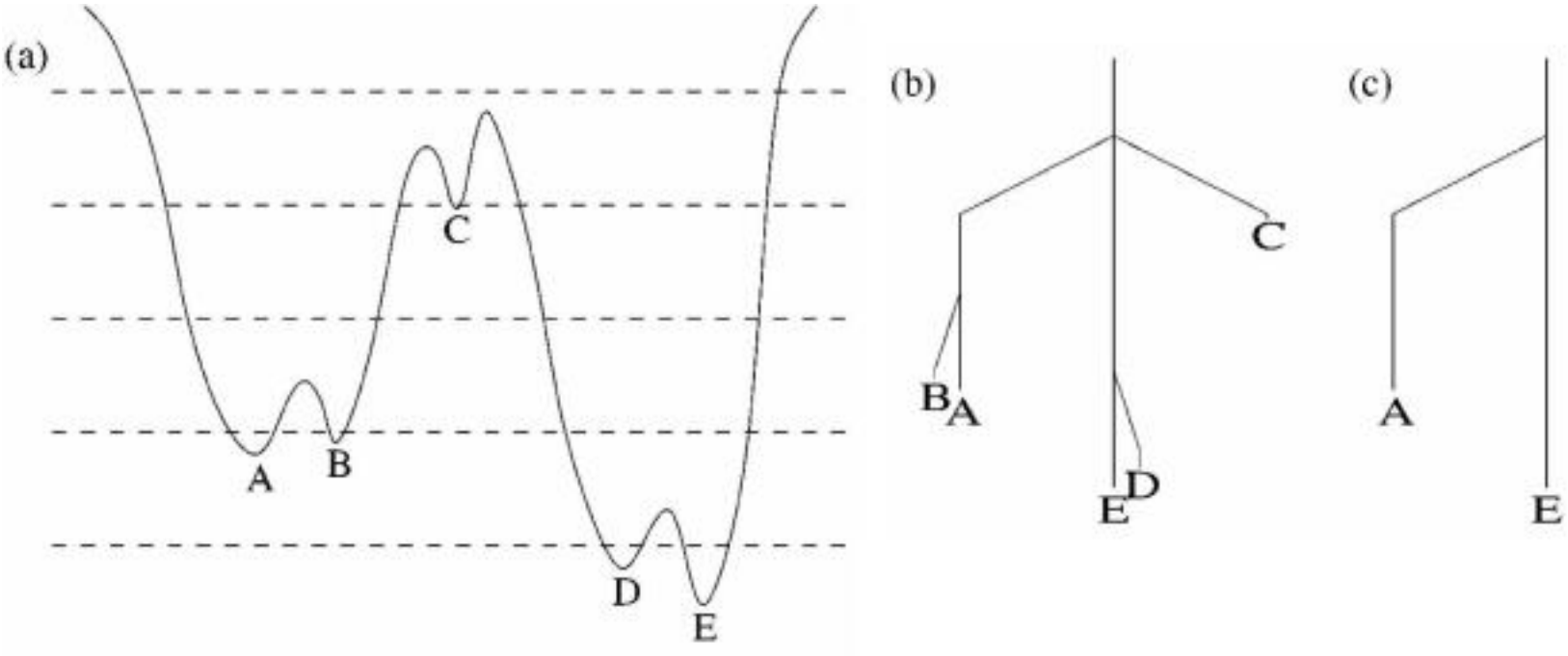


Basin Hopping in 2D

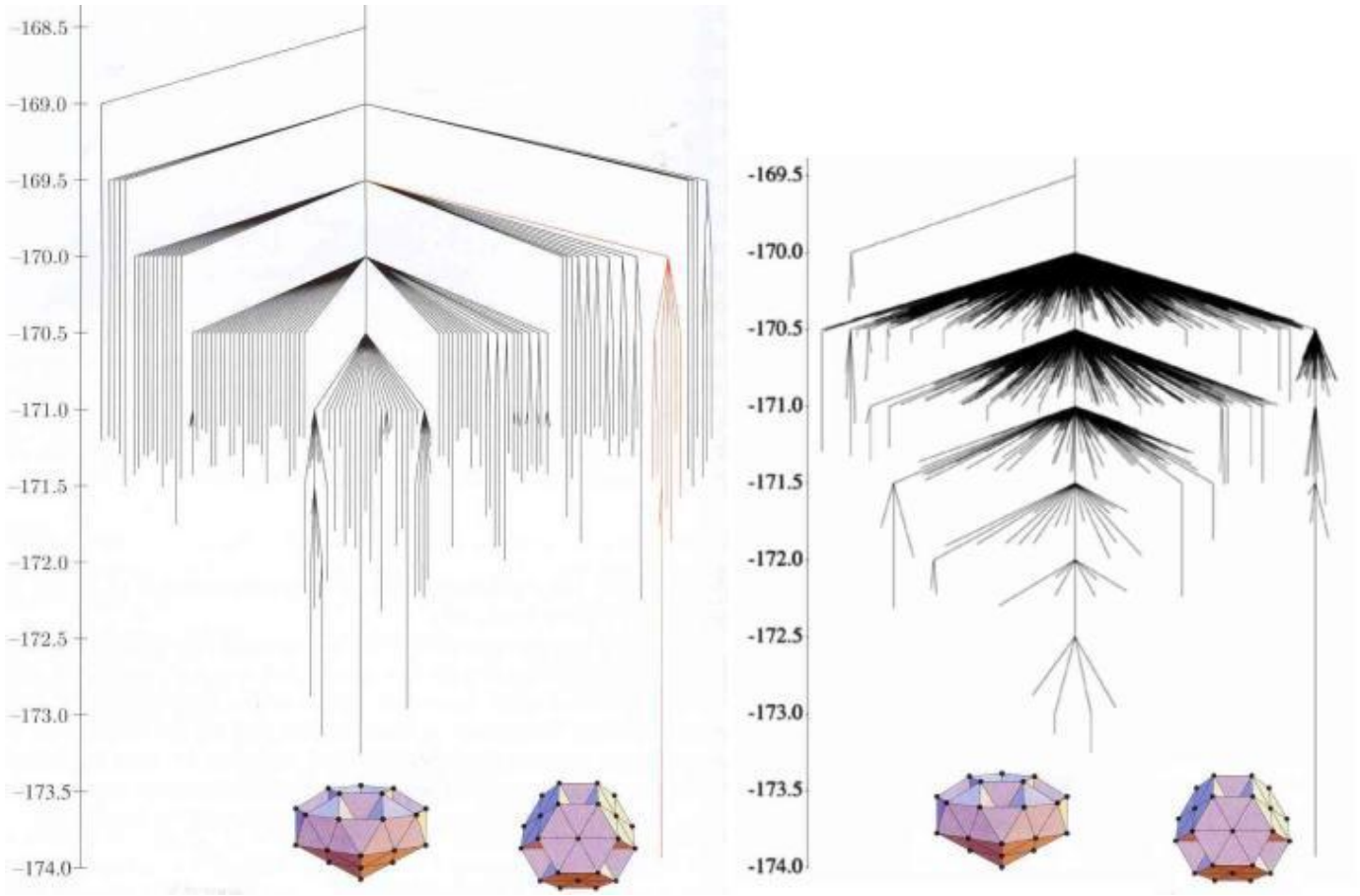




Basin Hopping and Disconnectivity Graphs



$N = 38$ Cluster with Basin Hopping



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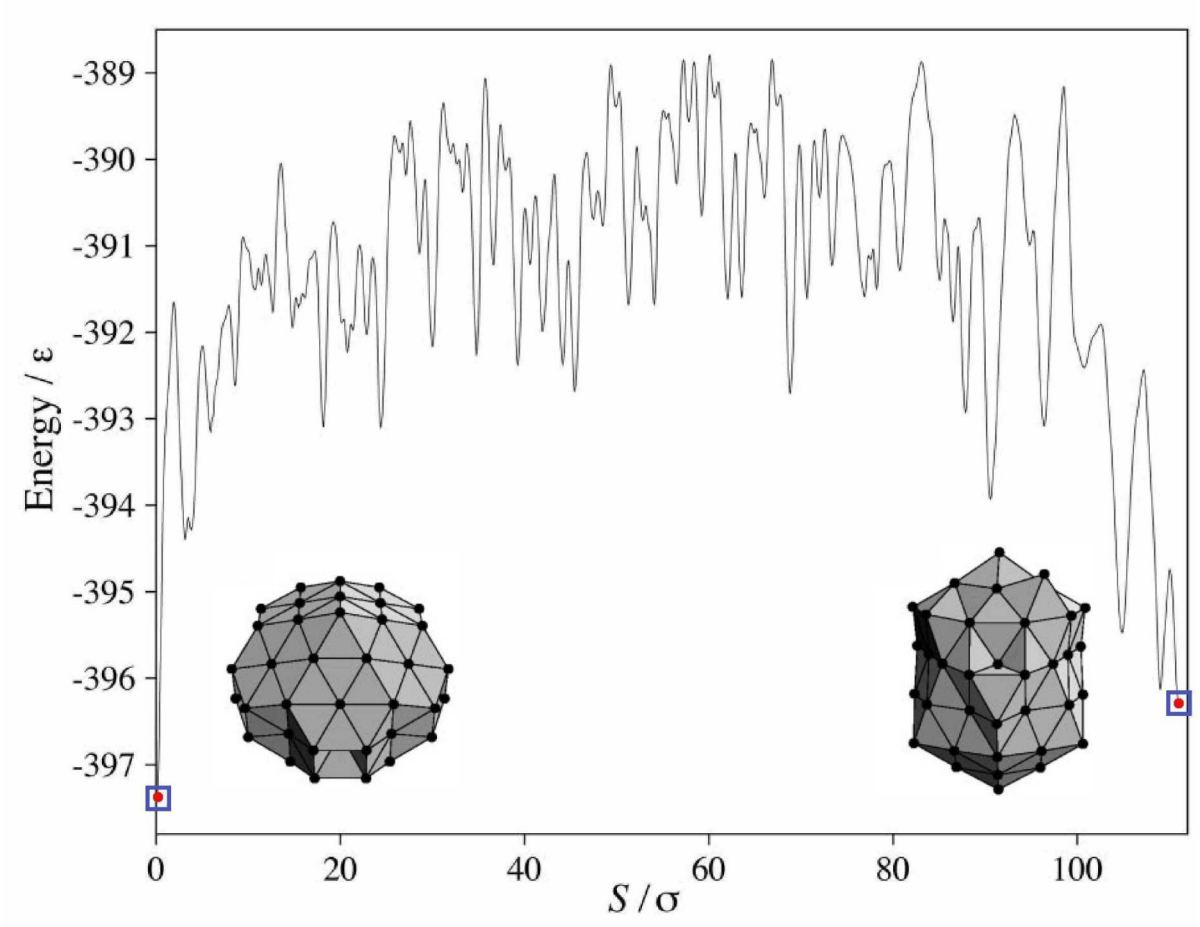
Applications

- Why search the whole of the PES?
  - do not only store the global minimum
  - the authors have a large database of all the local minima *and* the transition states between minima
- thus the lowest path between minima can be determined
- this is especially useful in the study of *protein folding*
  - more atoms $\Rightarrow$ many more local minima

Transition States



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My Research

- problem - optimisation of clusters
- technique - genetic algorithms
- testing of method - my program found global minimum of $N = 38$ cluster
- however - I do not require knowledge of the transition states or other local minima

Conclusions

- Cluster optimisation is a widely used method in the study of different systems, in this case, the potential energy surface.
- Disconnectivity graphs can be used to visualise a multi-dimensional PES.
- These can be simplified by use of an energy transform
  - basin hopping
- A database of structures can then be created which allows transitions between cluster minima to be determined.

Further Reading