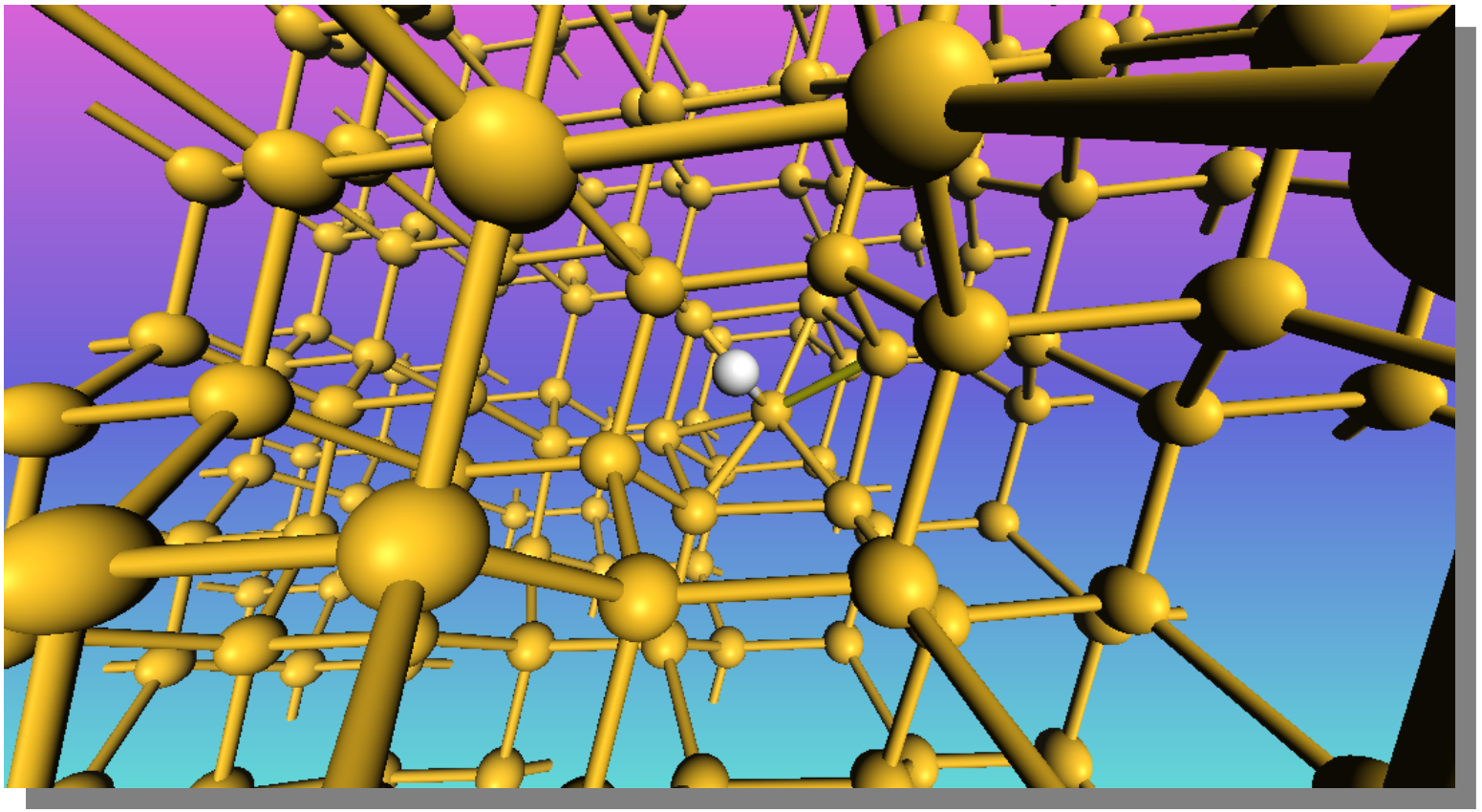
# Defects in semiconductors using random structure searching

*Andrew Morris*



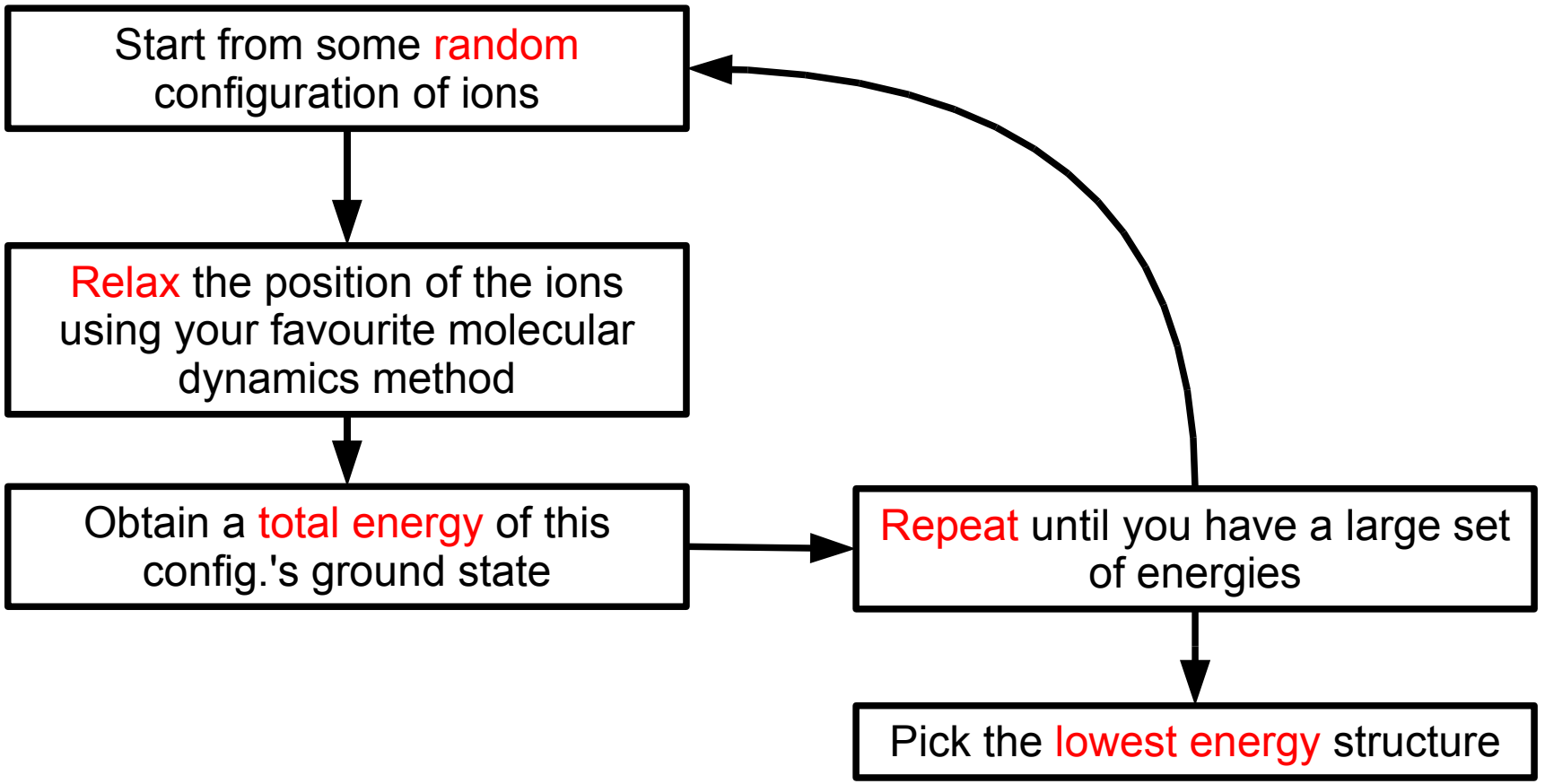
*Theory of Condensed Matter*
*Cavendish Laboratory*
*University of Cambridge*

# Outline

- What are Random Structure Searches?
- How do we apply them to defect problems?
- Fishing, Polishing and Embedding
- Digression into Multi-B Special K-point sampling
- Silicon Self-Interstitials - *A Test of the Method*
- Silicon and Hydrogen Interstitials - *A Demonstration of the Method finding new things*
- Relative stabilities – what actually forms?
- Conclusions

# What are Random Structure Searches?

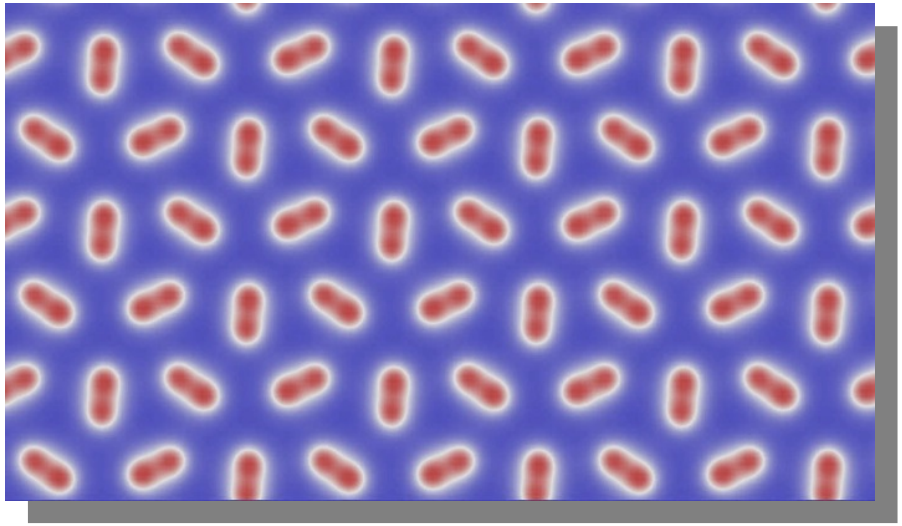
- Probably the most simple way to find the lowest energy structure of a solid



# Previous Successes

*When is H20 not water? CJP + RJN* *JCP 2007*

*Aluminium Hydride. CJP + RJN* *PRB 2007*



*Structure of phase III hydrogen. CJP + RJN*
*Nature Physics 2007*

*Graphite interlocation compounds GC + CJP + BDS + RJN* *PRB 2007*

*High Pressure Silane CJP + RJN* *PRL 2006*

# What about defects in Semiconductors?

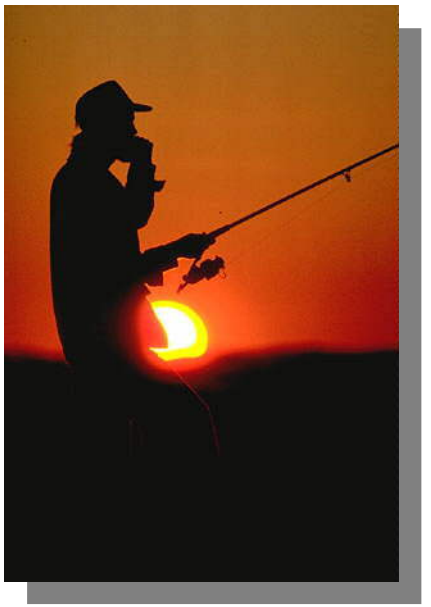
- Test calculations
  - *High Pressure Silane CJP + RJN* *PRL 2006*
- How do we modify the existing method to get accurate results for semiconductors?
- Start with every possible config. of the system, we must get the right answer

  Not Possible!
- How to create starting configs. that constrain the results?
- Make a hole in a perfect lattice ... more later

# Method

# The Method

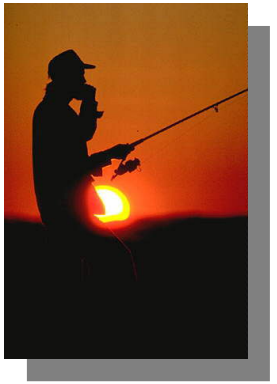
- Fishing



- Polishing

- Embedding

# Fishing



- Catch as many fish as you can.
  - Small cell 32-54 bulk atoms
  - 0.05eV/A force tolerance
  - Darwin (Supercomputer)

- Don't catch any red herrings.
  - Still has to be accurate : 2x2x2 Multi-B special k-point sampling (More Later)
    Good pseudopotentials
    DFT
    High planewave cutoff of basis set

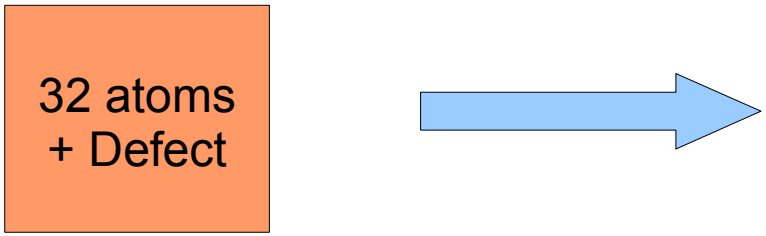
- Know when you've caught whopper.
  - Calculate space group symmetries
  - Good recognition of when two structures are the same

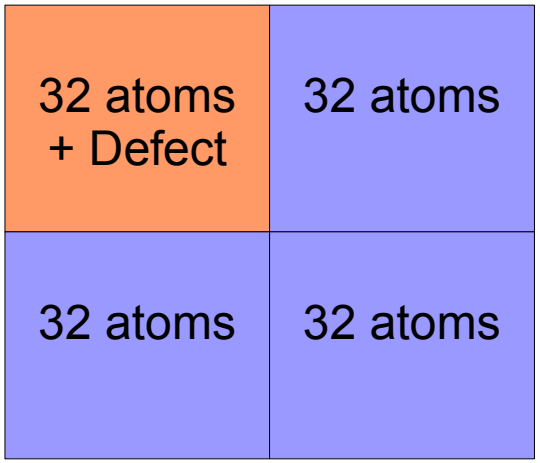
# Polishing

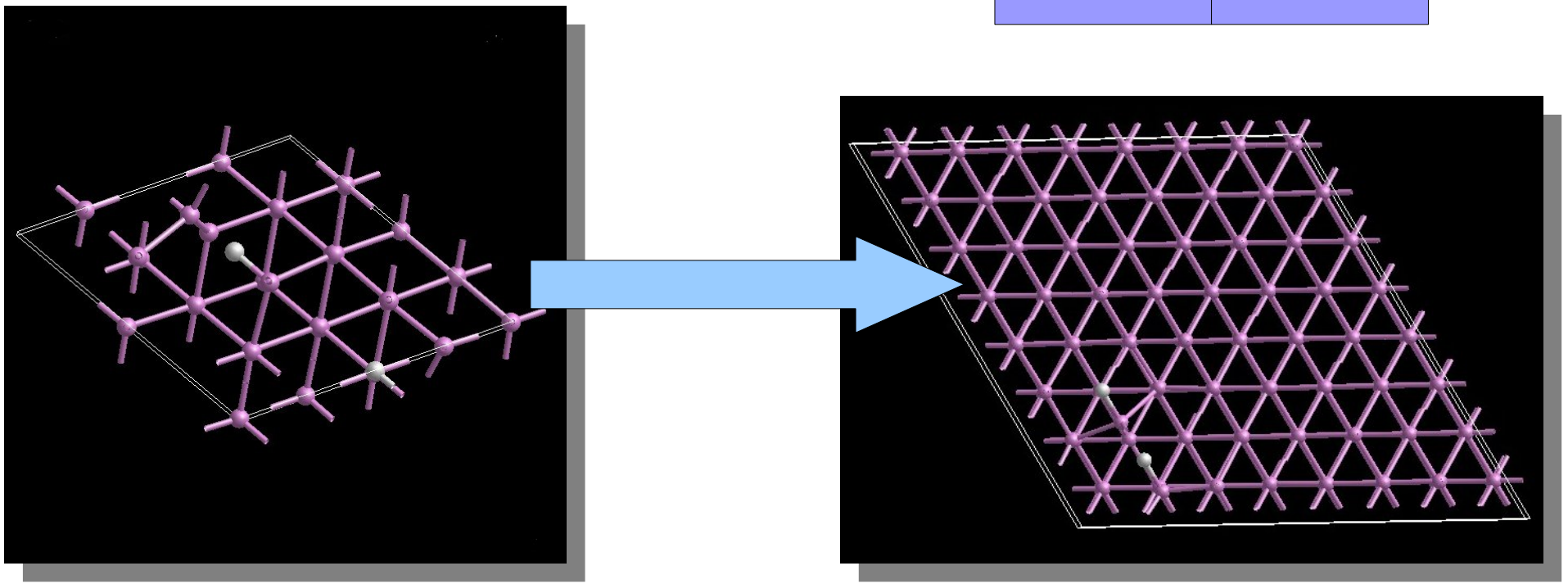
- Take:
  - The lowest energy structures
  - The high symmetry structures
  - Anything that looks interesting
- Do more DFT
  - High tolerance relaxation
  - OTF pseudopotentials
- Take *similutide.x86*
  - See what's well relaxed
  - See what structures are the same
    Even if they have different energies
    Even if they are of low symmetry

# Embedding

• A 32 atom cell is not large enough for an accurate total energy calculation. So we need to put the defect into a larger cell and relax further



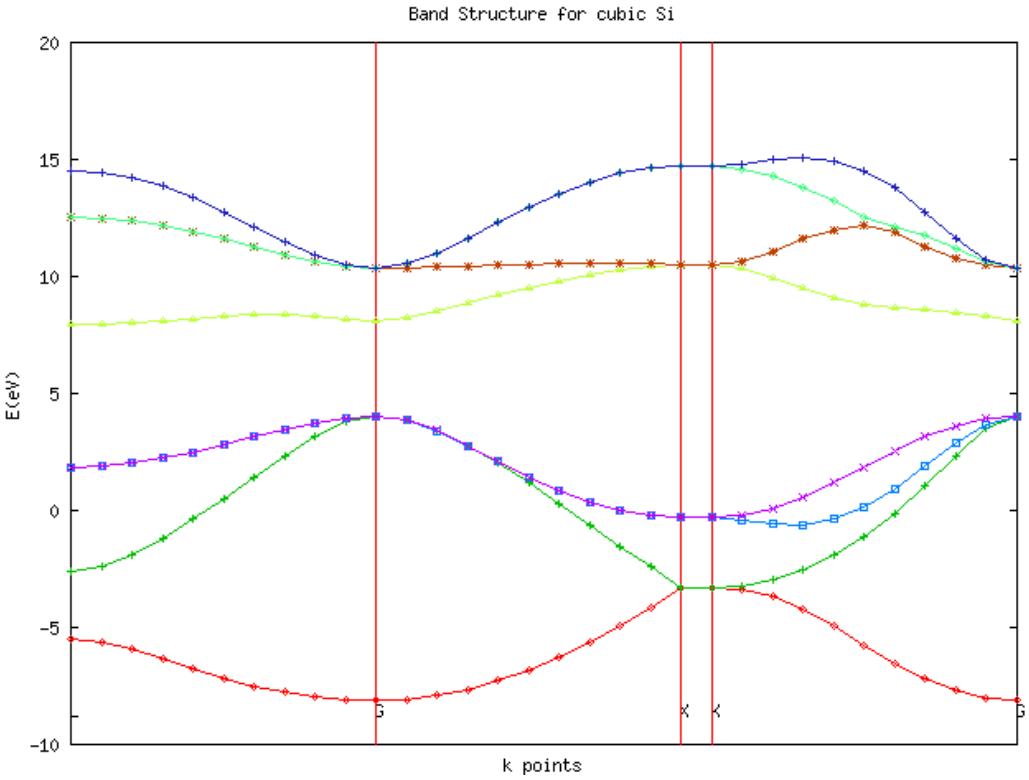
Electronic Structure Method
Search Method (Fishing / Polish / Embed)
K-point integration Method
Constraint Method

# Special K-point Sampling

# K-points

• In CASTEP we use plane-waves as a basis set for the electron's wavefunction. These are easy to represent in reciprocal space as k-points.

• In order to get the total energy of a crystal we must sum over all **k**, *i.e.* **k** in the first BZ. But **k** is continuous – so we need a way to approximate the integral.




D.J. Chadi and M.L. Cohen, *Tight Binding Calculations of the Valence Bands of Diamond and Zincblende Crystals.* Phys. Stat. Sol. (b) **68**, 405 (1975).

# Accuracy of Sums (from an example by MJR)

If E(k) is some 1-D function, real and symmetric about 0, (the Γ point), we can express this as the following Fourier series:

$$E(k) = b_0 + b_1 \cos\left(\frac{2\pi k}{G}\right) + \ldots$$

If E(k) is constant then the answer is $b_0$ any **k** will give the correct value. If not, we need to sample such that only the $b_0$ remains in the Fourier series, as all higher terms should integrate to 0.

Sample at k=0 :

$$E(k) = b_0 + b_1 \cos\left(\frac{2\pi 0}{G}\right) + \ldots = b_0 + b_1$$

Sample at k=G/4 :

$$E(k) = b_0 + b_1 \cos\left(\frac{2\pi}{G}\frac{G}{4}\right) + \ldots = b_0$$

So different k-points give different answers!

# Baldereschi's Mean-Value Point

There is some point in the 1st BZ that gives the best approximation to an integral over all the BZ.

This is in terms of the first-failure star - the first G vector that gives rise to an error in the integration.

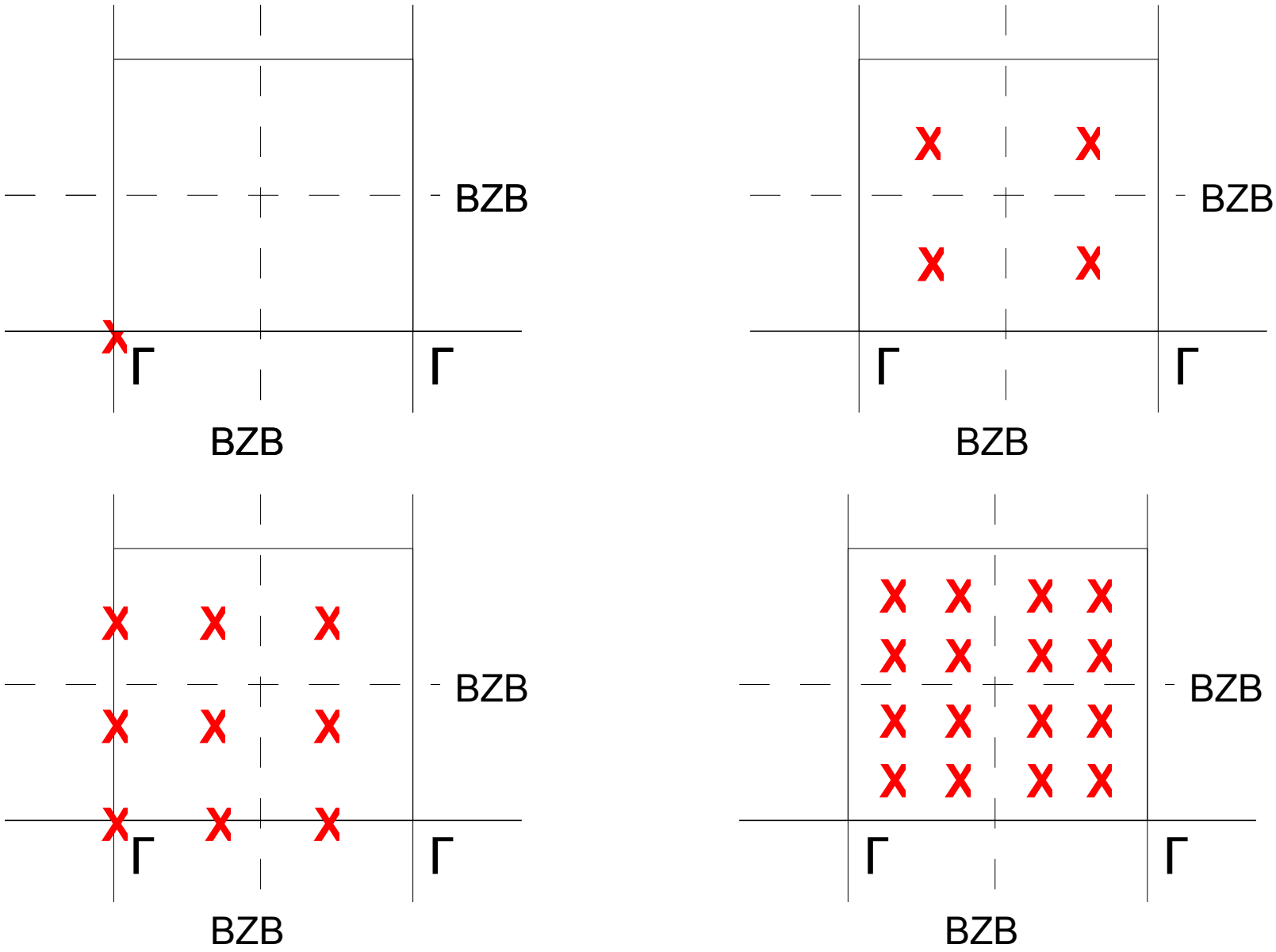
Further to this, Baldereschi minimises the error in the first-failure star.

In the old days, when you could only afford one k-point, the Baldereschi was the best.

# Monkhorst and Pack

If you have more than one k-point, where do you put them to get the best answer?

# Monkhorst and Pack

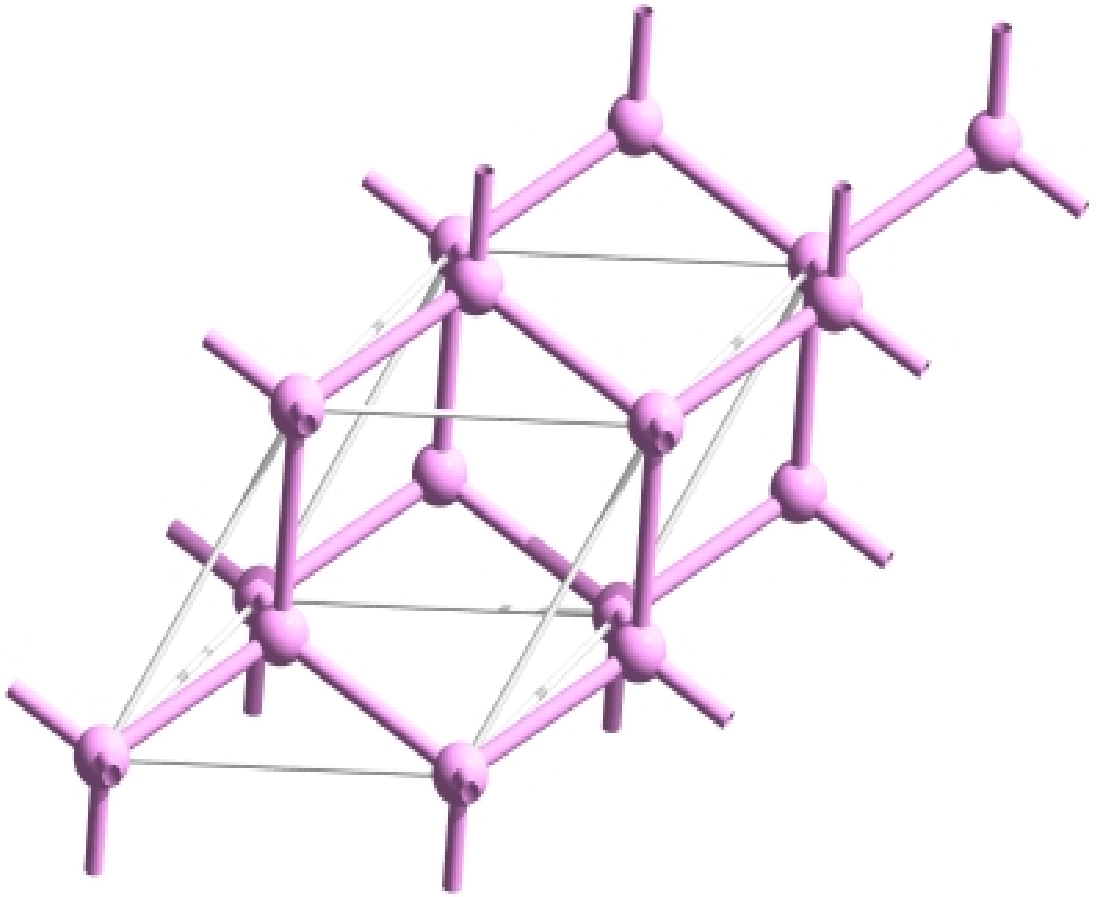


# MP an example

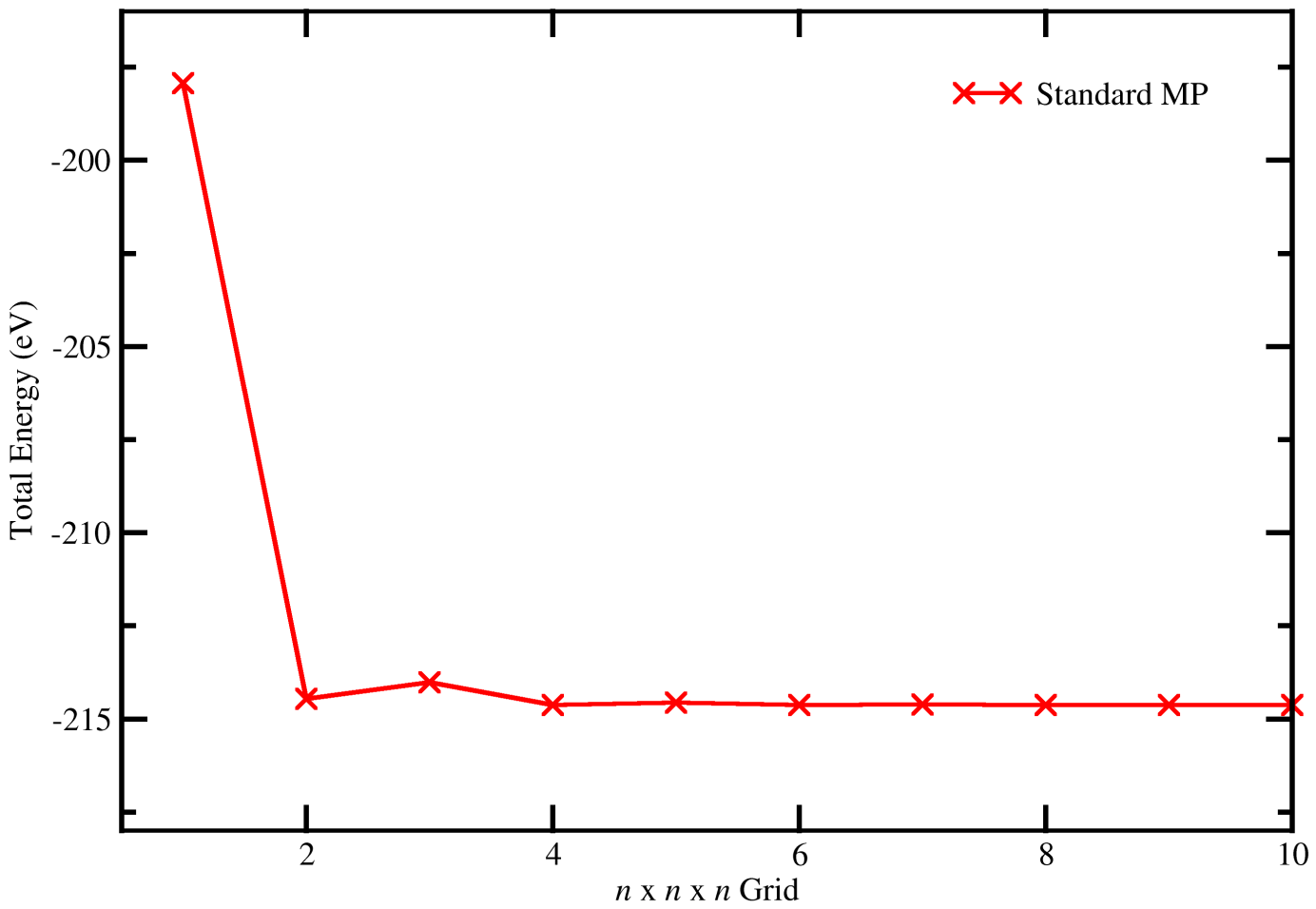
Our example system is Silicon with 2 atoms in the unit cell.

This cell is FCC.

We increase the standard MP grid in CASTEP from 1x1x1 to 10x10x10



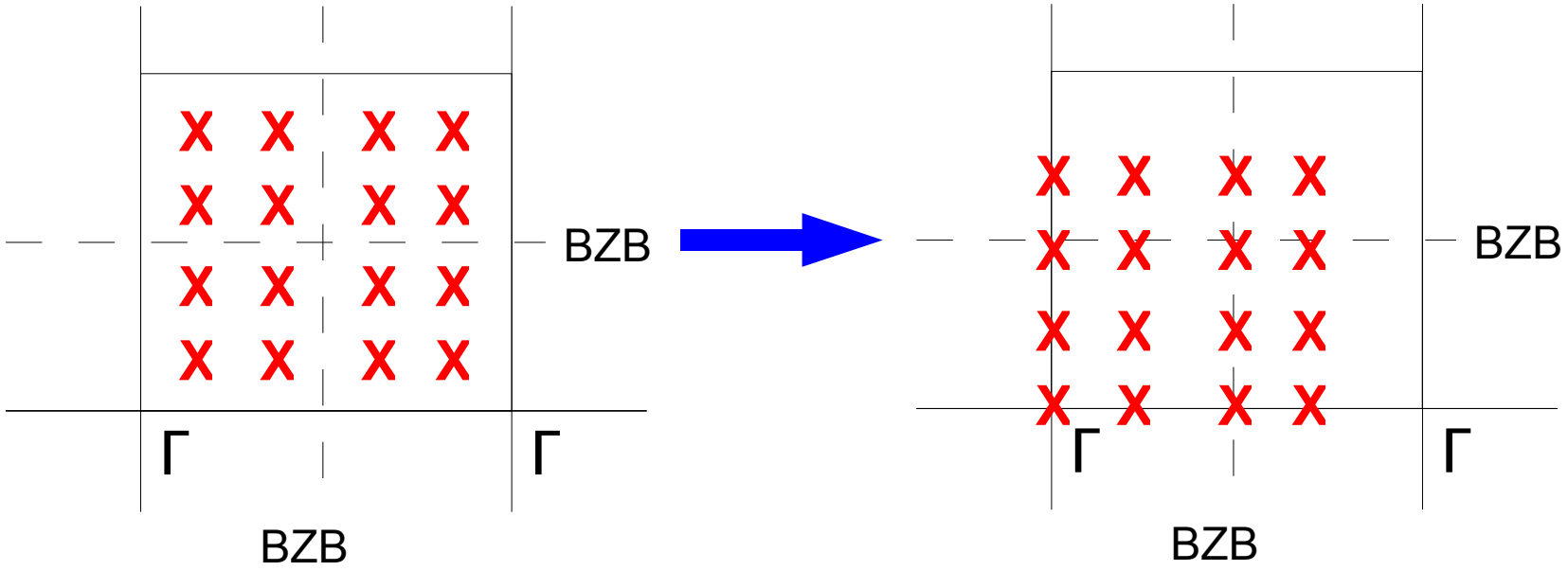
# Standard MP a la CASTEP



# How can we improve?

The wiggliness of the line is due to some grids being centred on Γ and some not.

We could force all of the grids to have a point at Γ. *(i.e.* shift all the even grids)



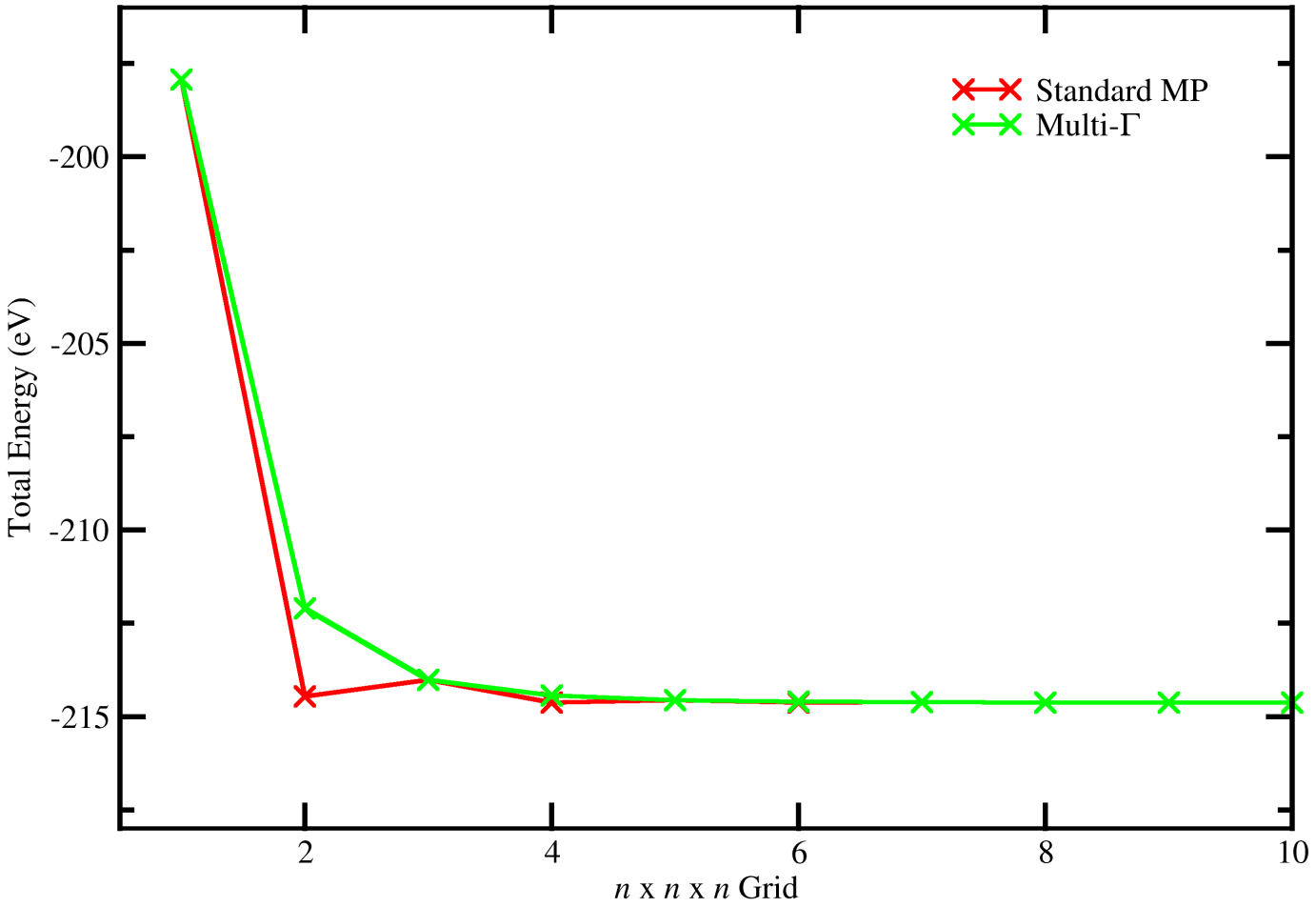

It might not be as good – as it has a point at Γ.

Will probably break the symmetry generation -

- my geom. opt. cells don't have symmetry anyway.

But at least it would be systematic.

# MP with all grids shifted to Γ

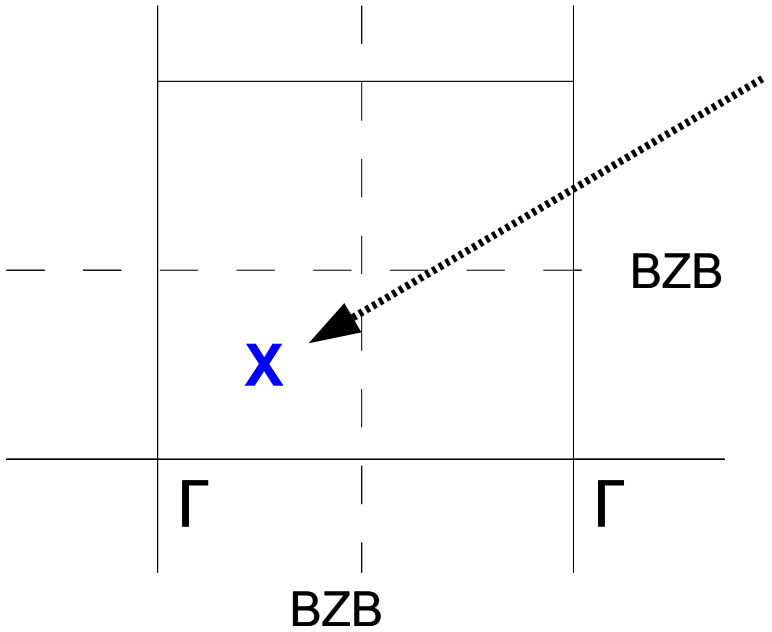


# Back to Baldereschi

So we know now we must keep the grids centred on one point if we want smooth convergence.

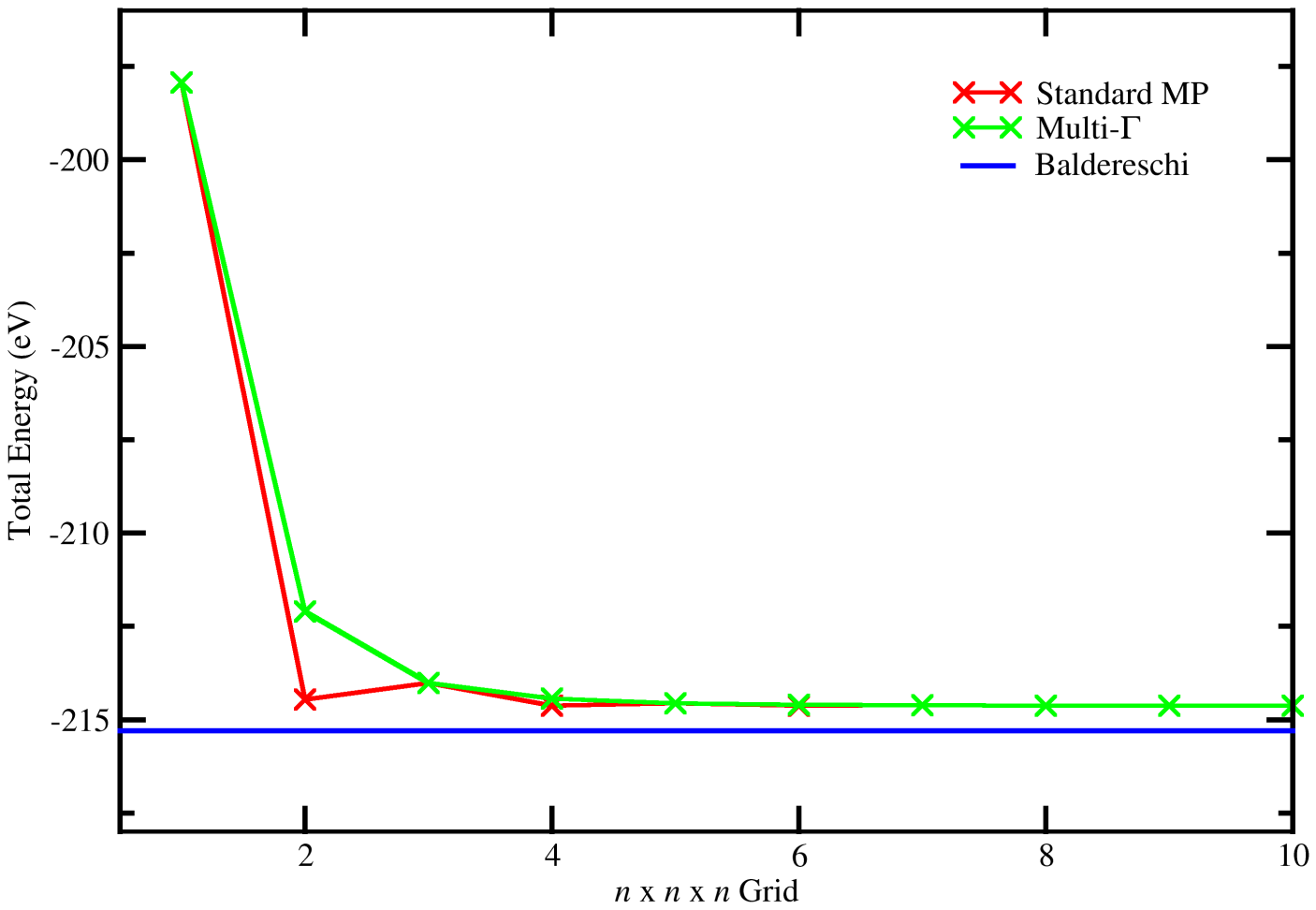
So how does the Baldereschi point do?

1 x 1 x 1 grid (*i.e.* 1-kpoint)




Baldereschi of SC cell (1/4, 1/4, 1/4 )

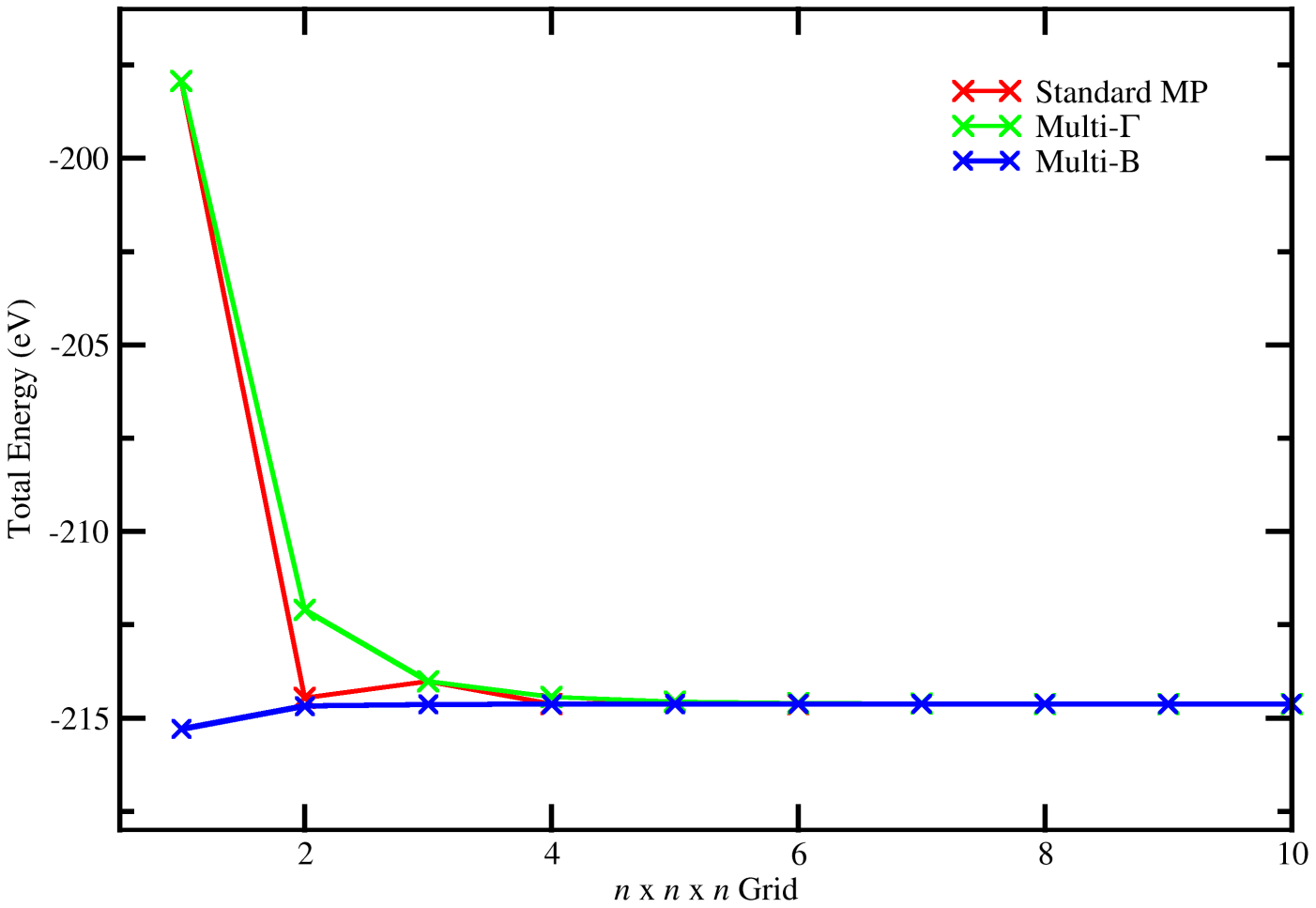
# Baldereschi



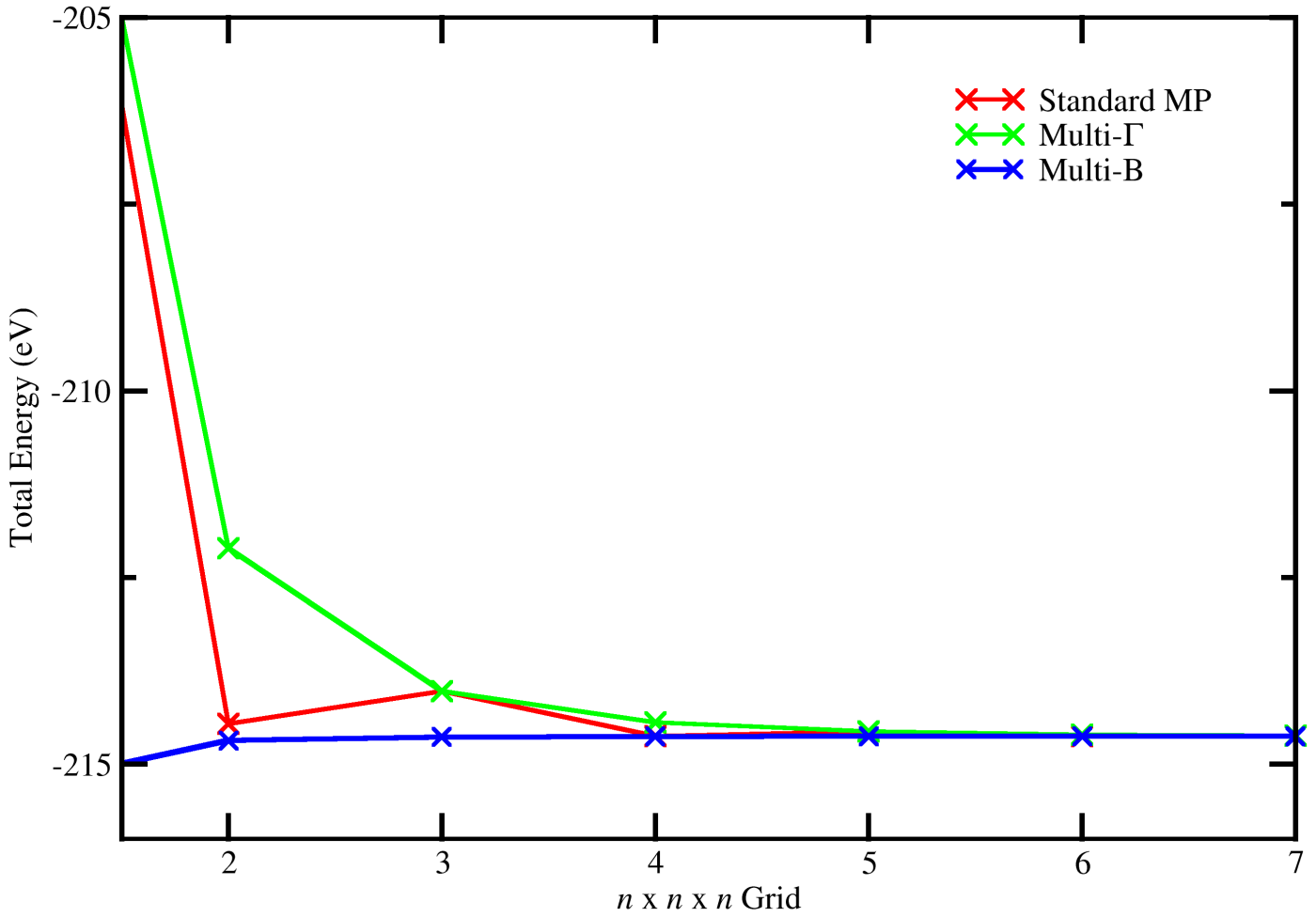
# Can we do any better?

Baldereschi and Monkhorst and Pack?

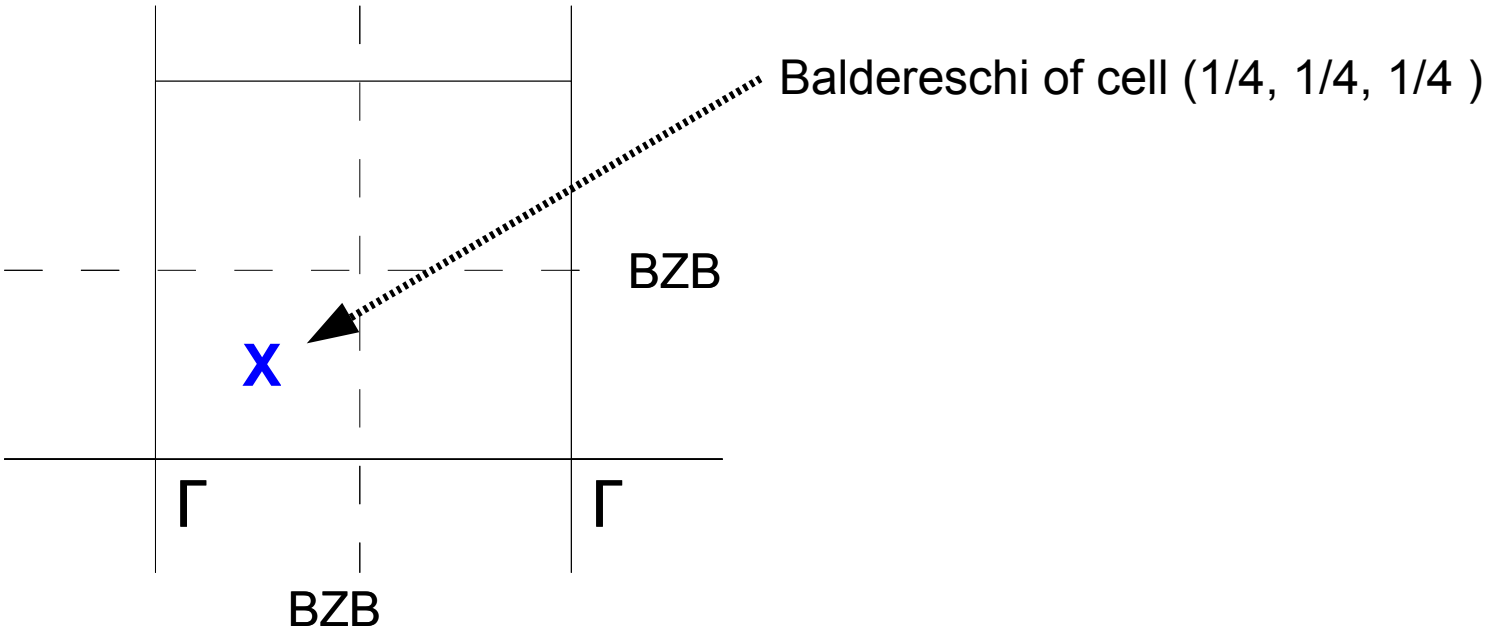
# Baldereschi + MP grid



# Baldereschi + MP grid

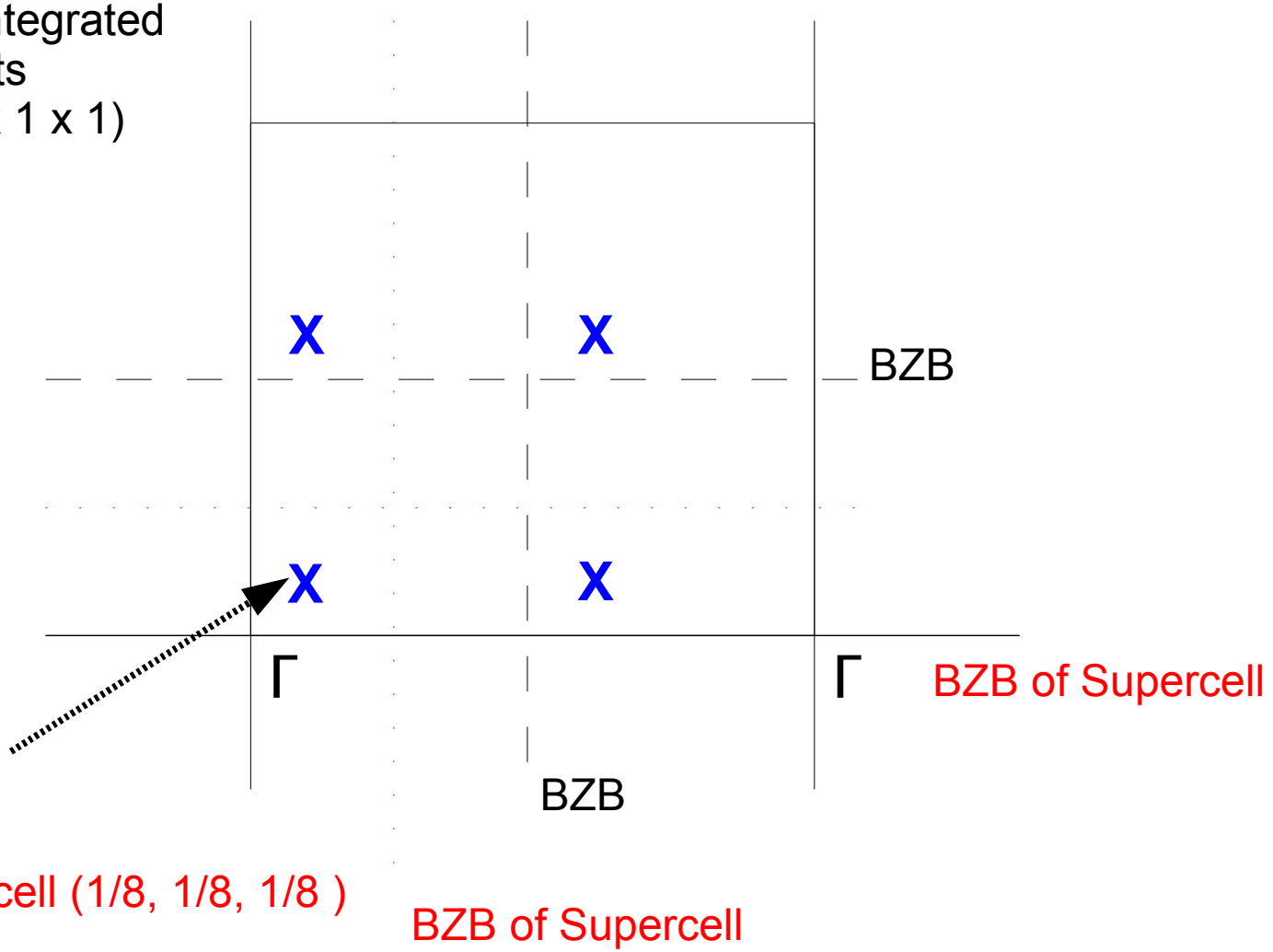


# How?



# How?

We have effectively integrated the Silicon 16 cell at its Baldereschi point (1 x 1 x 1)




Normal MP 2 x 2 x 2 grid, but centred on Baldereschi of super cell (1/8, 1/8, 1/8 )

# Conclusions

If you can have only one k-point. Surely the Baldereschi point is best.

If you have symmetry in your system, and need lots of k-points, you probably need standard MP using Symmetry to reduce the k-point set.

Use Baldereschi + MP to economically sample bigger super-cells. (Useful in QMC).

(The QMC project I have going is using this method)

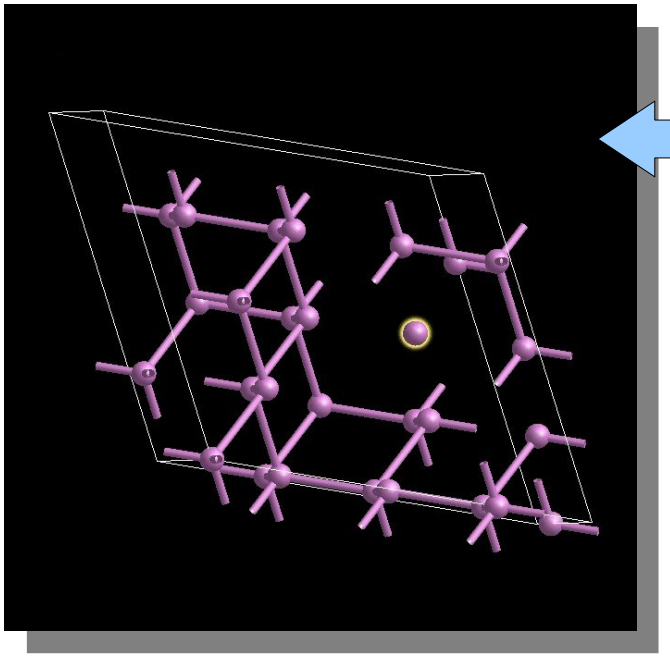
Electronic Structure Method
Search Method (Fishing / Polish / Embed)
K-point integration Method
Constraint Method

# Silicon with Silicon Interstitials

## A Test

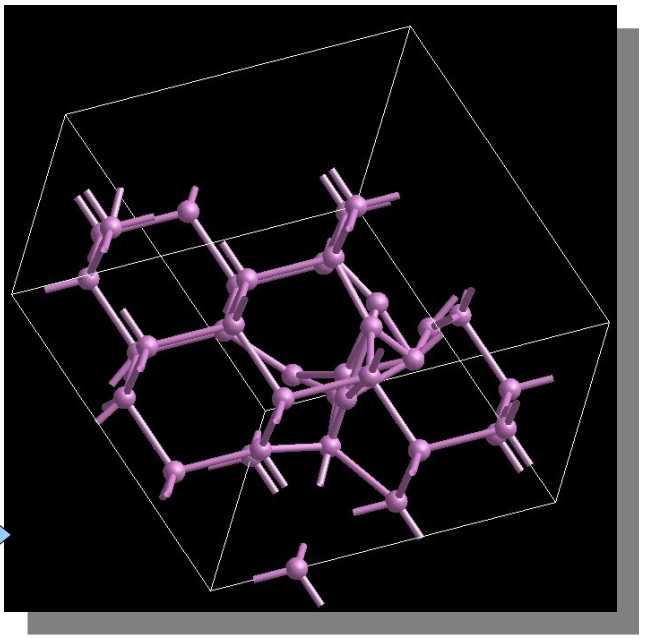
# Constraints

- Want to constrain the search.
- Do this by keeping the bulk intact and creating a hole of randomness.
- For example: Silicon self-interstitial
  - Bulk 54 atoms.
  - Remove 5 atoms from the bulk
  - Fish

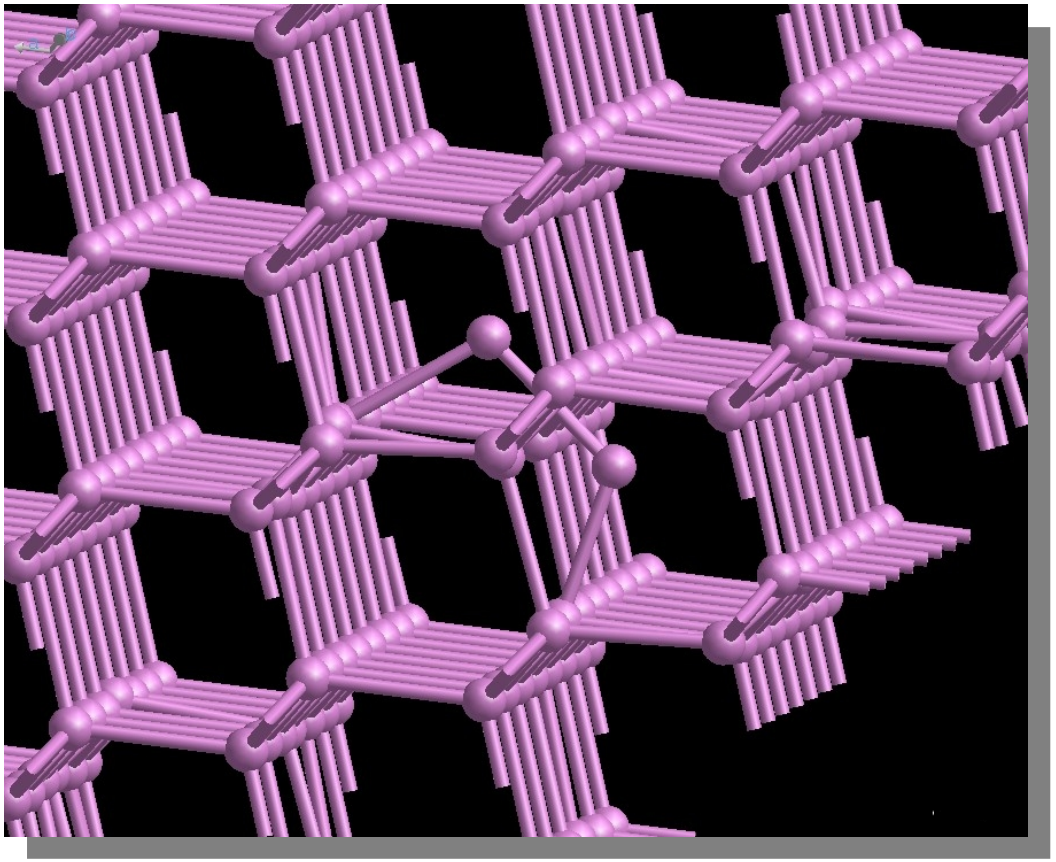


Hole

Initial positions before randomisation



# Silicon with 1 extra Silicon



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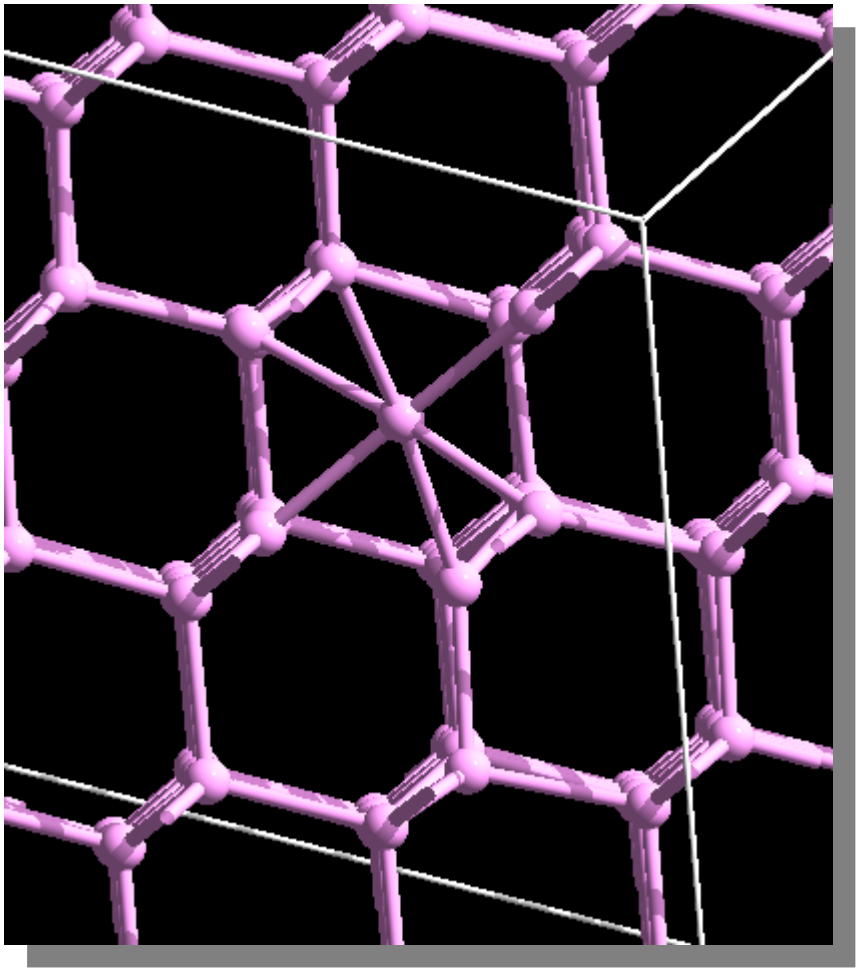

Hexagonal

- Find both ground state structures quite easily.

Electronic Structure Method
Search Method (Fishing / Polish / Embed)
K-point integration Method
Constraint Method

Ready!

# Silicon with Silicon and Hydrogen Interstitials

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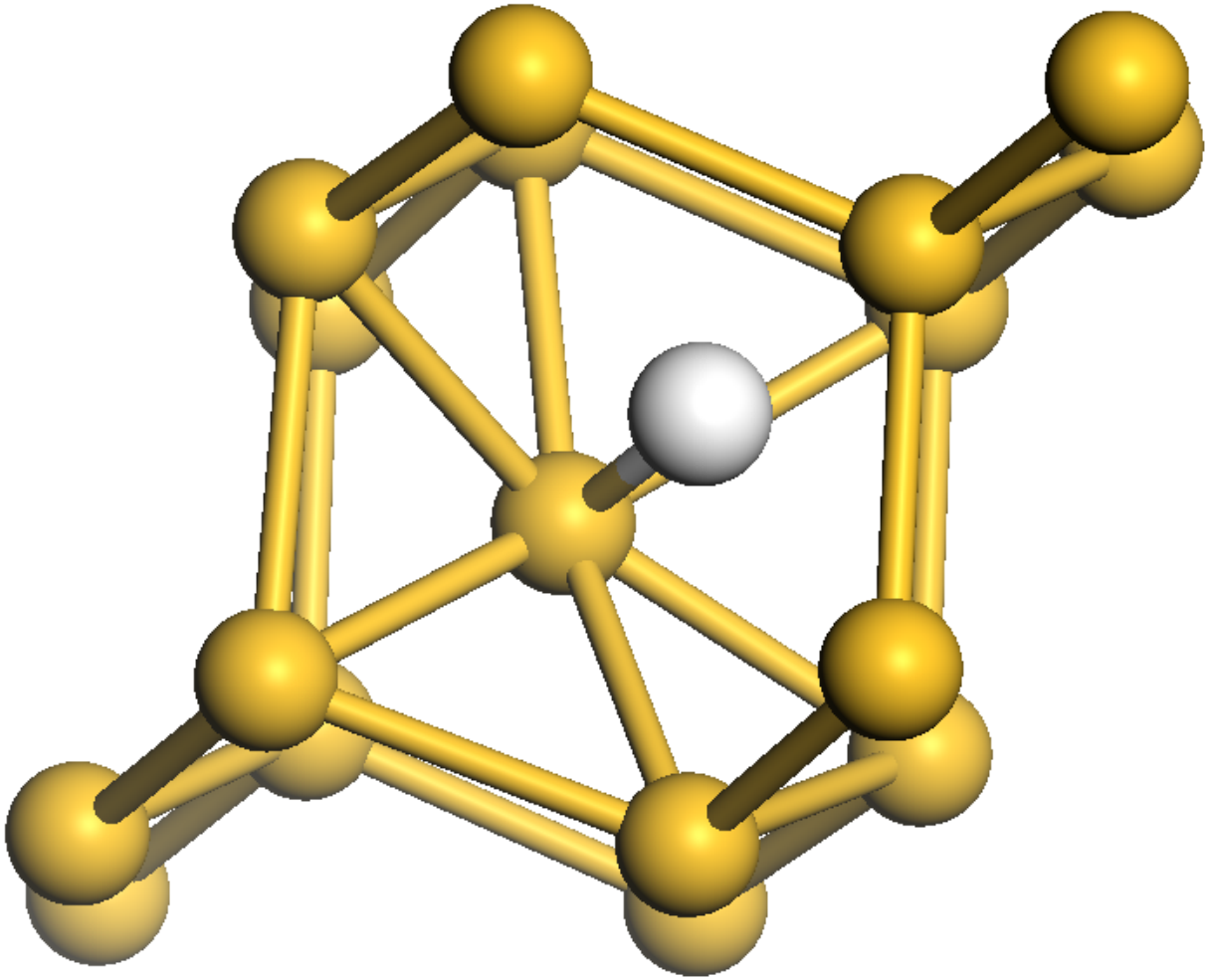
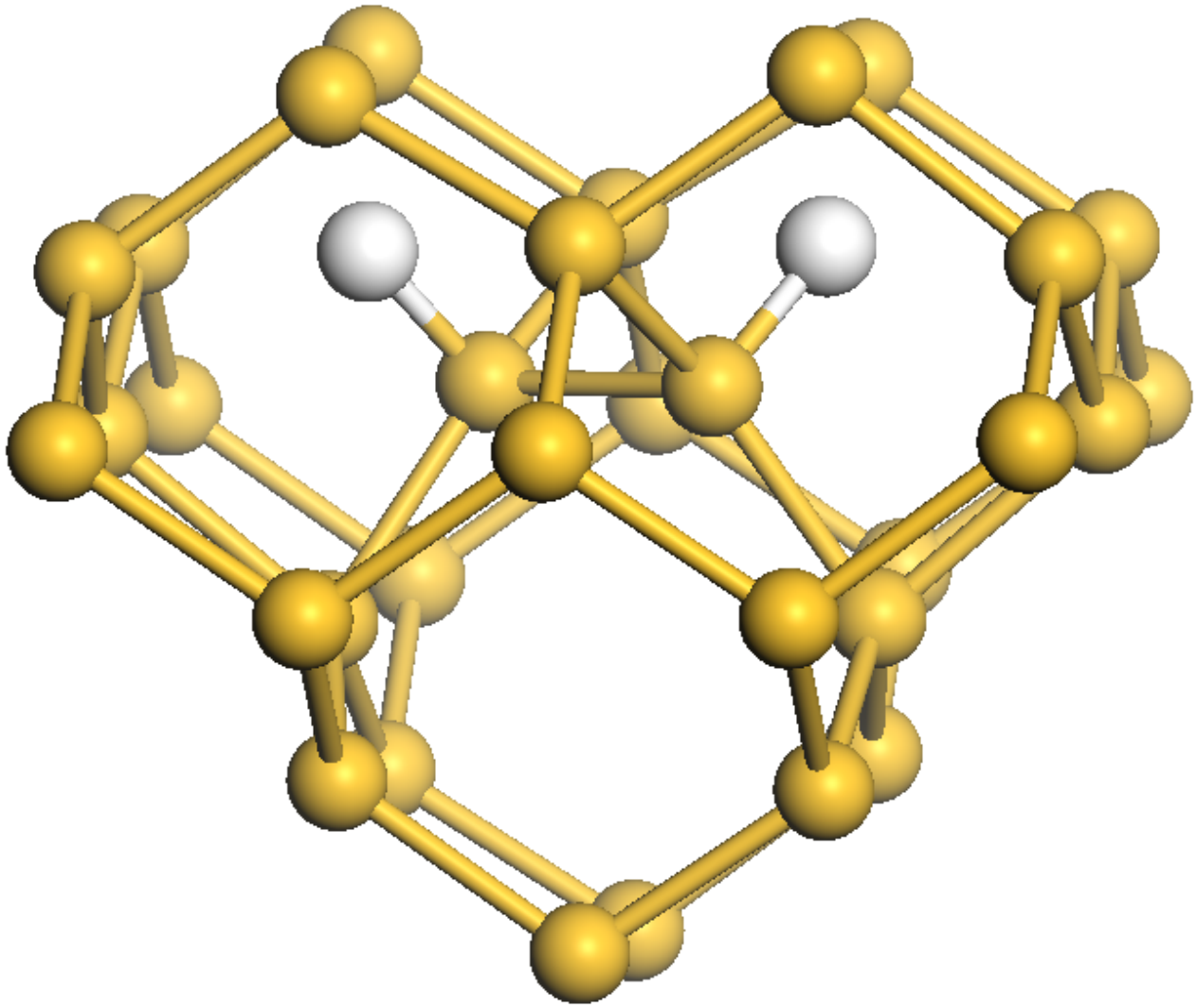
# Silicon with 1 extra Si and 1,2,3 or 4 Hydrogen

- Can use small cells
- Hydrogen changes energy states can get activation and passivation from H impurities
- Not fully understood. Only one defect so far found by experiment
- Some previous studies, carried out from symmetry arguments

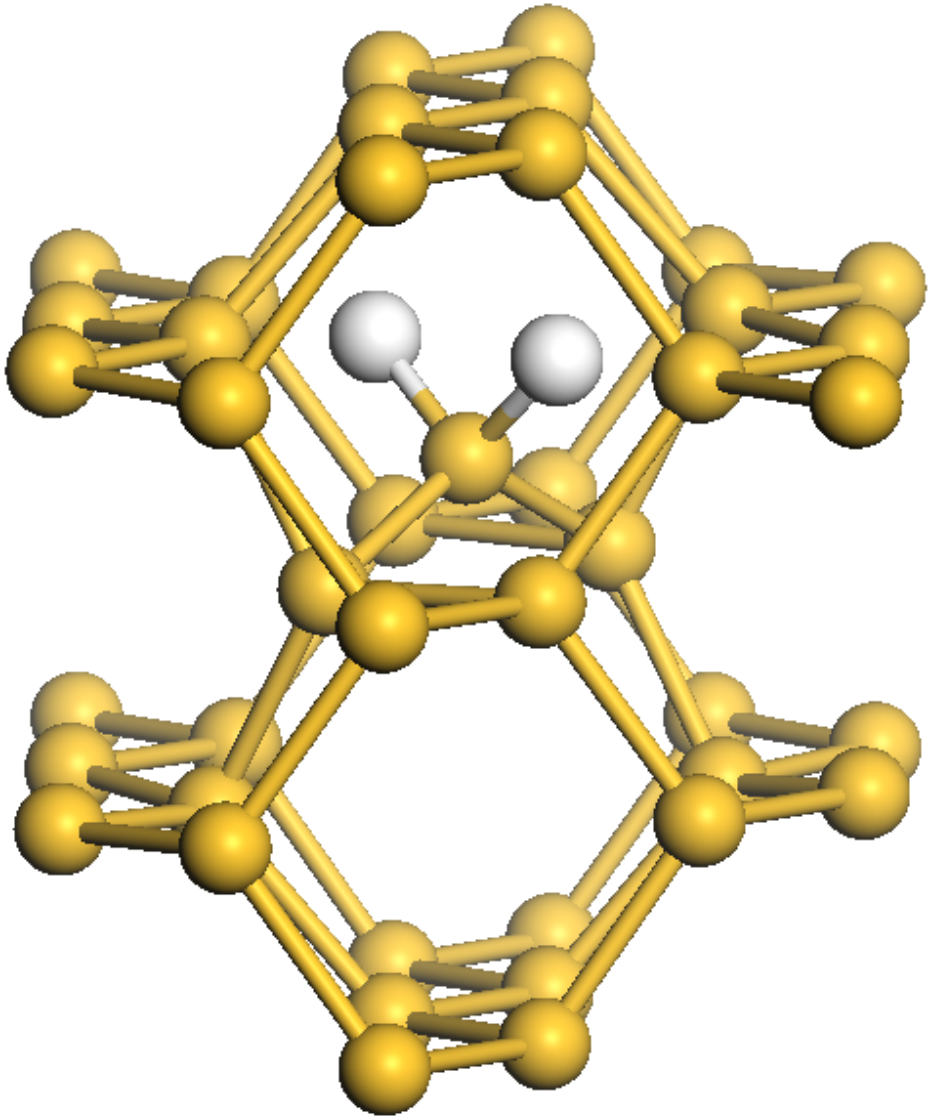
# Silicon with 1 extra Silicon and 1 Hydrogen



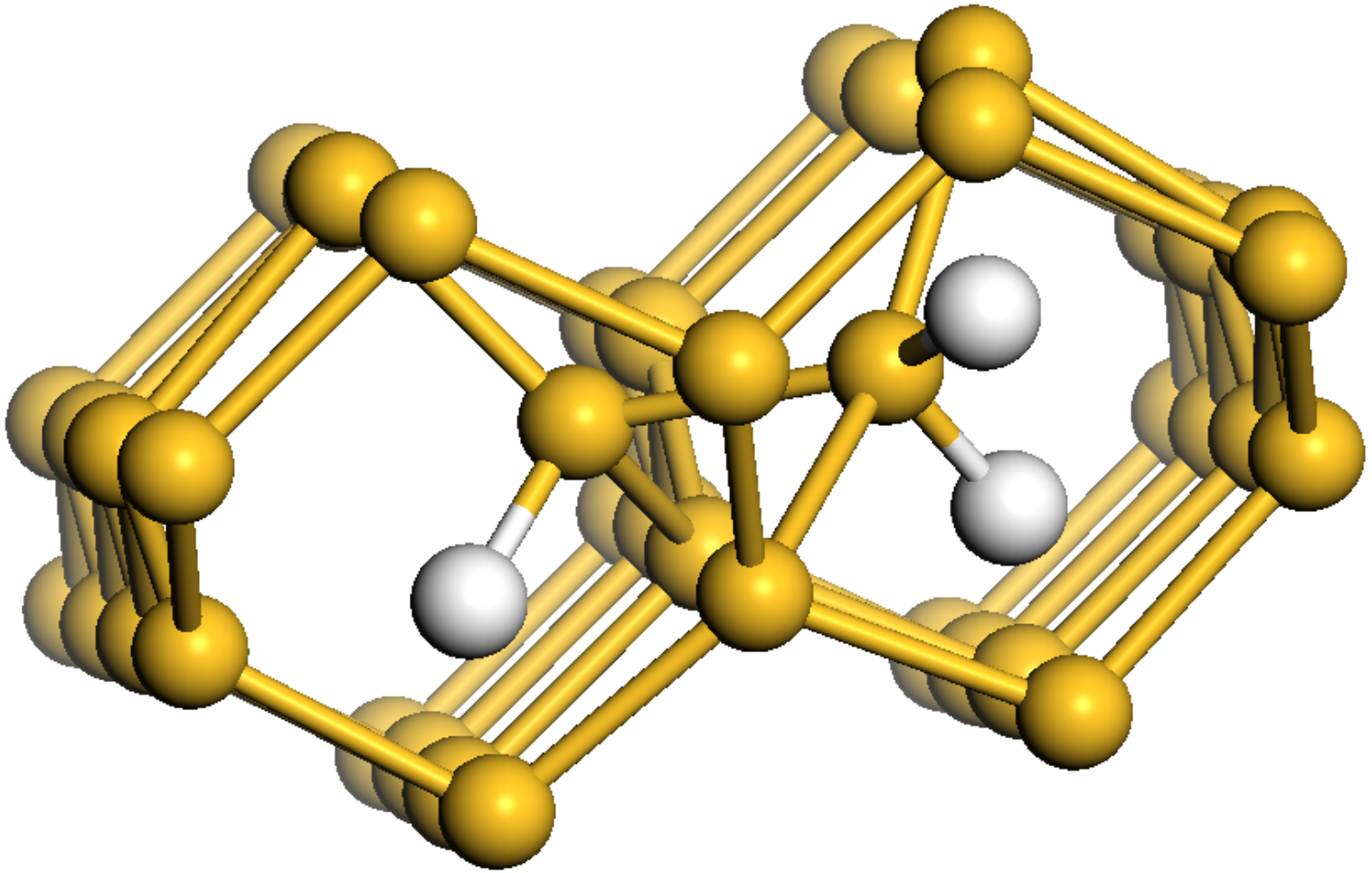
# Silicon with 1 extra Silicon and 2 Hydrogen



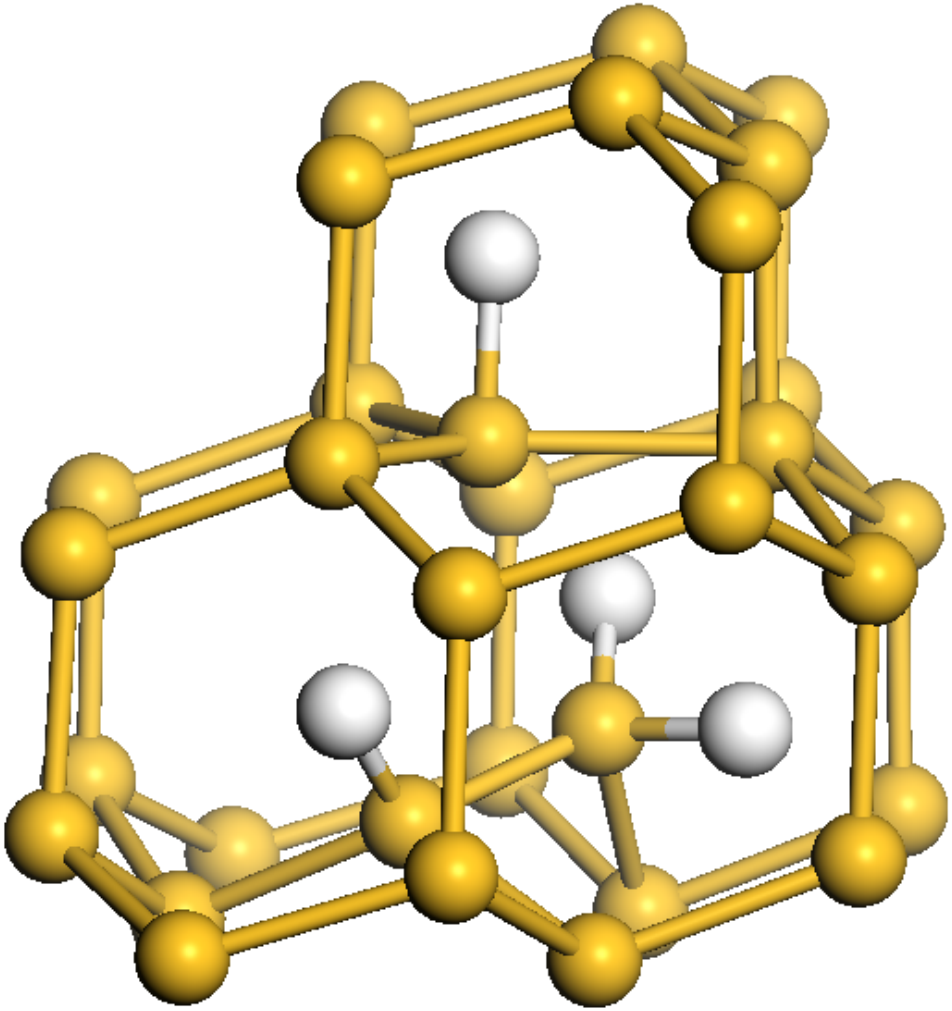
# Silicon with 1 extra Silicon and 2 Hydrogen*



# Silicon with 1 extra Silicon and 3 Hydrogen



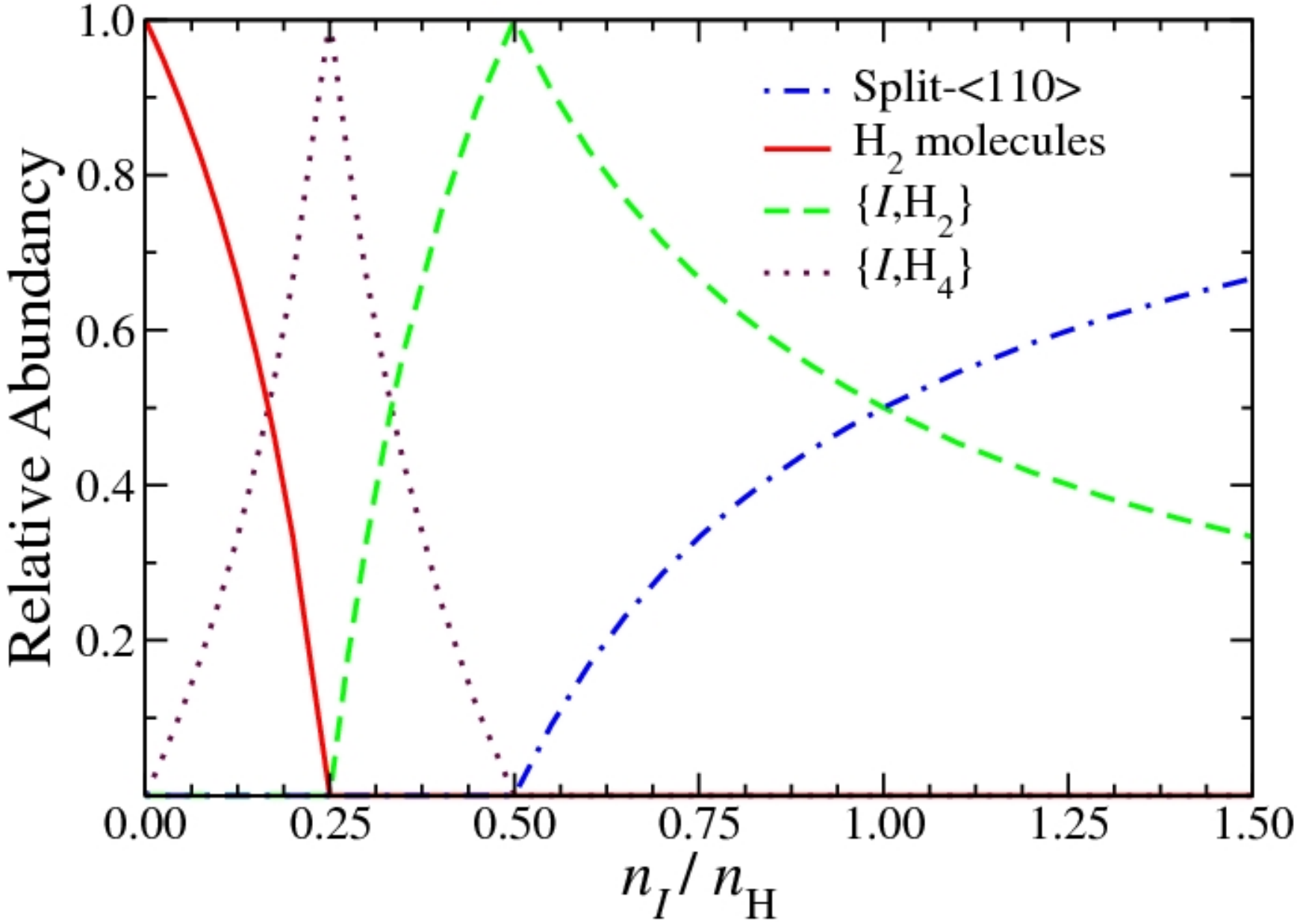
# Silicon with 1 extra Silicon and 4 Hydrogen



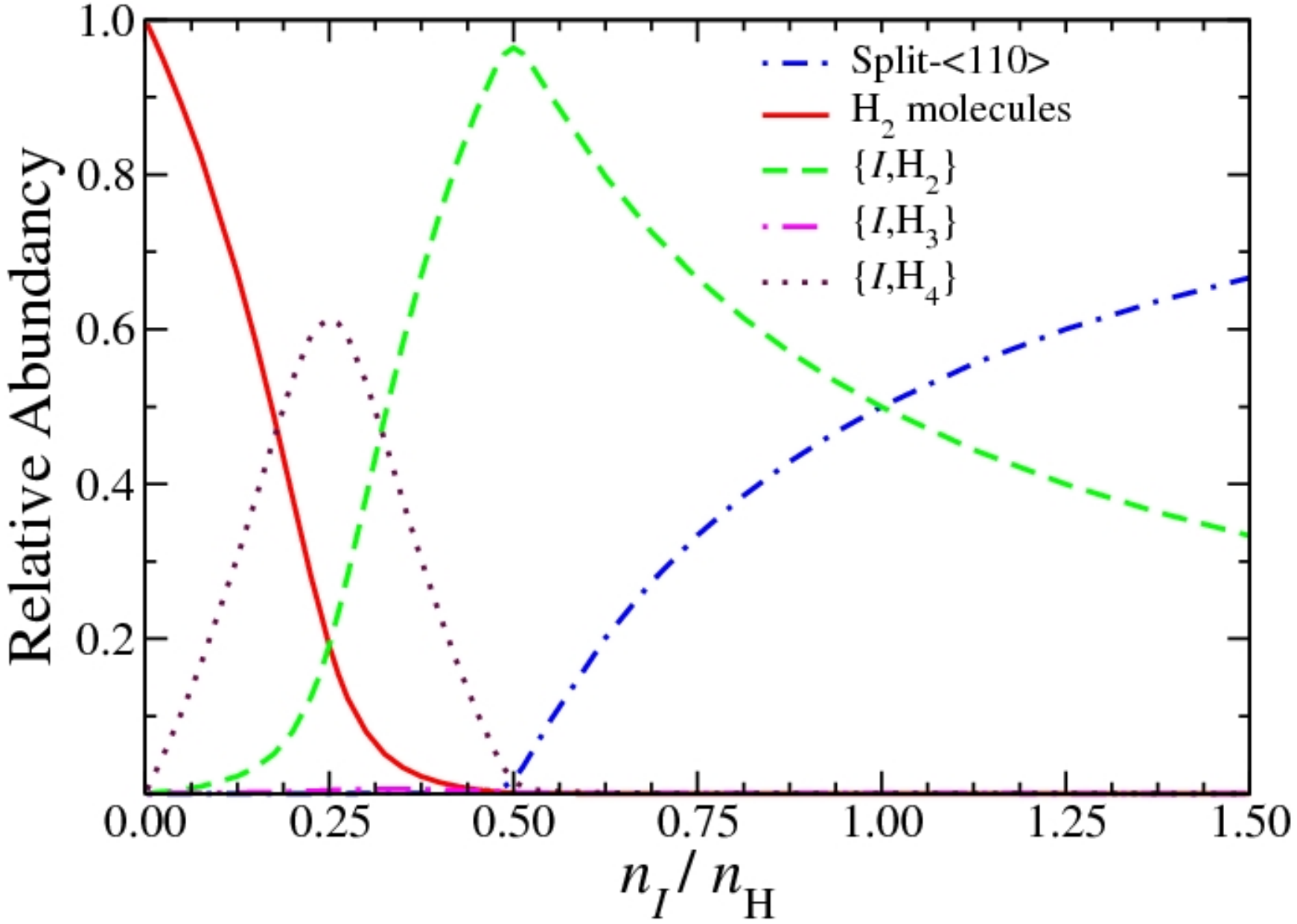
# Problems and Tweaks

- Difficult to find the I+H2 ground state from a 5 atom hole.
- Tried again from a 1 atom hole.
- Get the right I+H2 defect quite quickly.
- Have also tried 1 atom holes from hexagonal site. Good results.

# Relative Abundancies (T=0)



# Relative Abundancies (T=1200K)



# Conclusions

Random Structure Searching in Defects works, and can reproduce results found by other methods.

Can also find gain new insights into the defects that form

Get all of the metastable defects for free

We have a method now, that can generate results quickly
Fish / Polish / Embed

Constraints are important to reduce the search space.

Start with a small hole on a well-defined site and randomise.

The beauty of the method is in the the simplicity of the algorithm

Unlike other methods, we don't have to think up starting configs. that bias the results.

# Acknowledgements