

# Geometry Optimisation

Dr Jonathan Skelton

Department of Chemistry, University of Manchester  
([jonathan.skelton@manchester.ac.uk](mailto:jonathan.skelton@manchester.ac.uk))

- Geometry optimisation in the bulk
  - Theory
  - Geometry optimisation in VASP
- Theory vs. experiment
  - Choice of exchange-correlation functional
- Troubleshooting: what to do when things go wrong
- Phonon calculations (if time permits)
  - Imaginary modes, dynamical stability and mode mapping

Slides online: <https://tinyurl.com/y6l6r6jg>



## Problem:

Find the set of atomic positions  $\mathbf{R} = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$  and lattice vectors  $\mathbf{a} = \{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$  that define the minimum (a stationary point) on the potential-energy surface

## Key parameters:

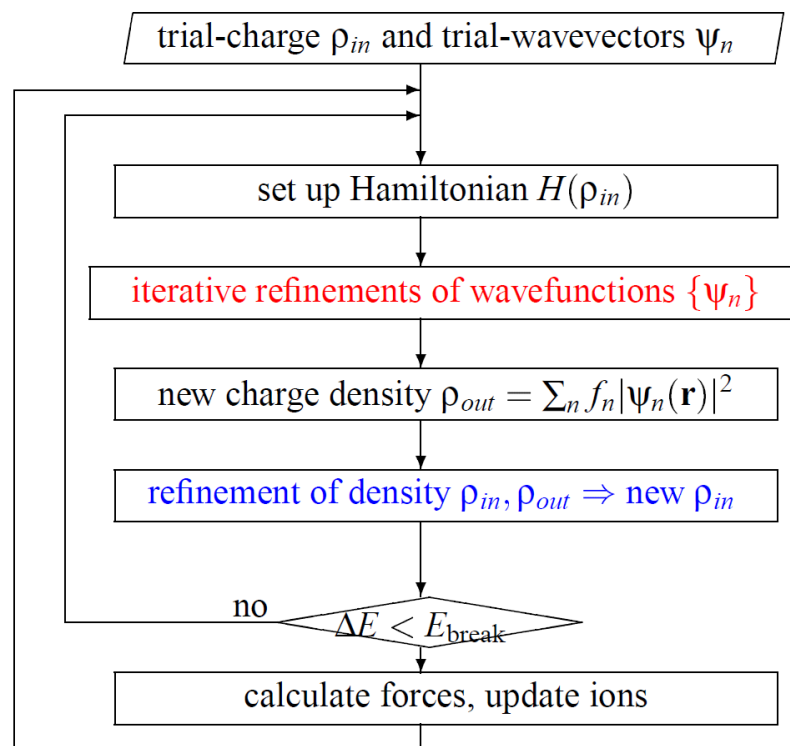
$$\mathbf{F}_N = -\frac{\partial E_0}{\partial \mathbf{r}_N} = -\left\langle \Psi_0(\mathbf{R}, \mathbf{a}) \left| \frac{\partial H(\mathbf{R}, \mathbf{a})}{\partial \mathbf{r}_N} \right| \Psi_0(\mathbf{R}, \mathbf{a}) \right\rangle$$

$$\sigma_{ij} = -\frac{\partial E_0(\mathbf{a})}{\partial \epsilon_{ij}} = -\left\langle \Psi_0(\mathbf{R}, \mathbf{a}) \left| \frac{\partial H(\mathbf{R}, \mathbf{a})}{\partial \epsilon_{ij}} \right| \Psi_0(\mathbf{R}, \mathbf{a}) \right\rangle$$

## Approach:

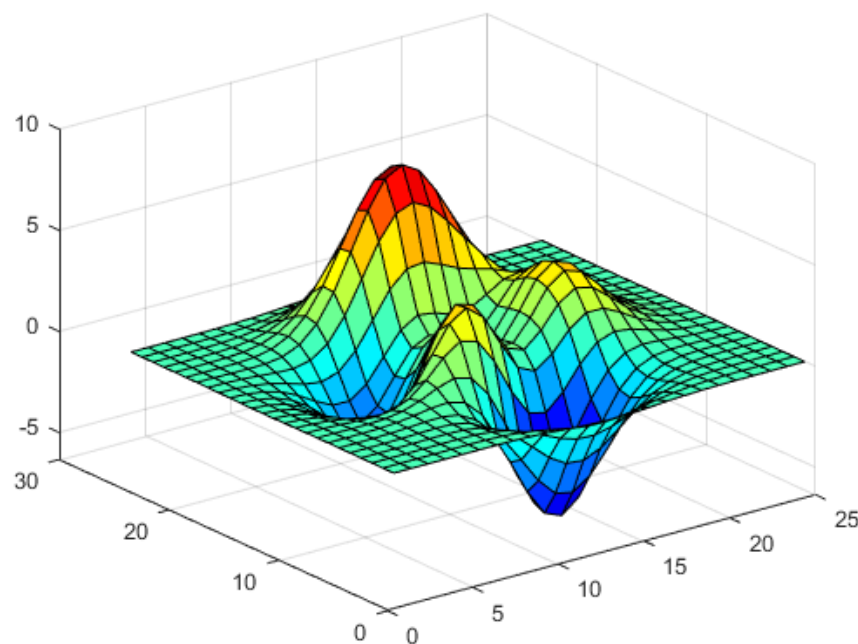
Adjust an initial  $\mathbf{R}$  and  $\mathbf{a}$  to minimise  $E_0$ ,  $\mathbf{F}_N$  and/or  $\sigma_{ij}$  *via* an optimisation algorithm

[https://www.vasp.at/vasp-workshop/slides/dft\\_introd.pdf](https://www.vasp.at/vasp-workshop/slides/dft_introd.pdf)



<https://www.vasp.at/vasp-workshop/slides/optelectron.pdf>

- In general, performing a geometry optimisation involves using an algorithm to locate a minimum on a multidimensional potential-energy surface (PES)



<https://www.mathworks.com/help/matlab/visualize/creating-3-d-plots.html>

# The steepest descent algorithm

## Problem:

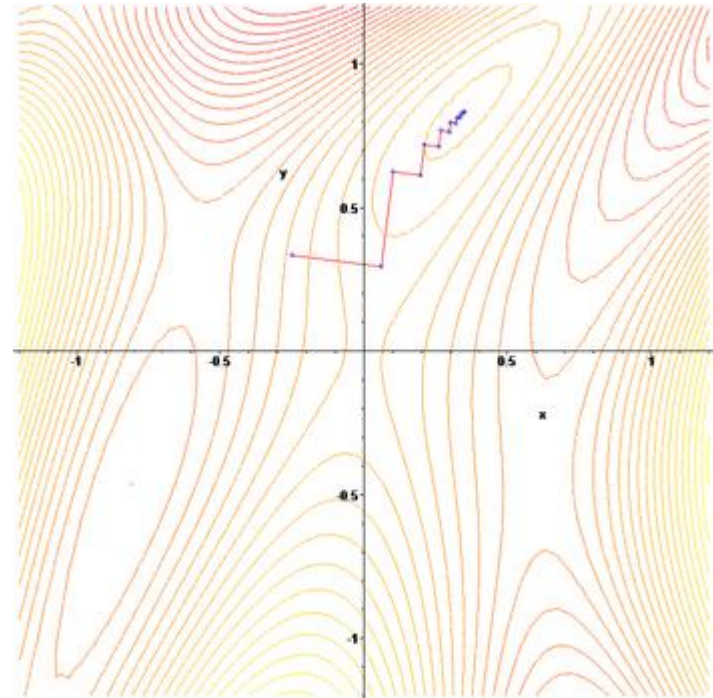
Follow the forces/stresses to the nearest minimum

## Solution 1 - Steepest Descent:

$$\mathbf{R}_{n+1} = \mathbf{R}_n - \gamma \nabla E(\mathbf{R}_n) = \mathbf{R}_n + \gamma \mathbf{F}(\mathbf{R}_n)$$

## Pros and cons:

Slow “zig-zag” convergence to the minimum; requires many iterations



[https://en.wikipedia.org/wiki/Gradient\\_descent](https://en.wikipedia.org/wiki/Gradient_descent)

## Problem:

Follow the forces/stresses to the nearest minimum

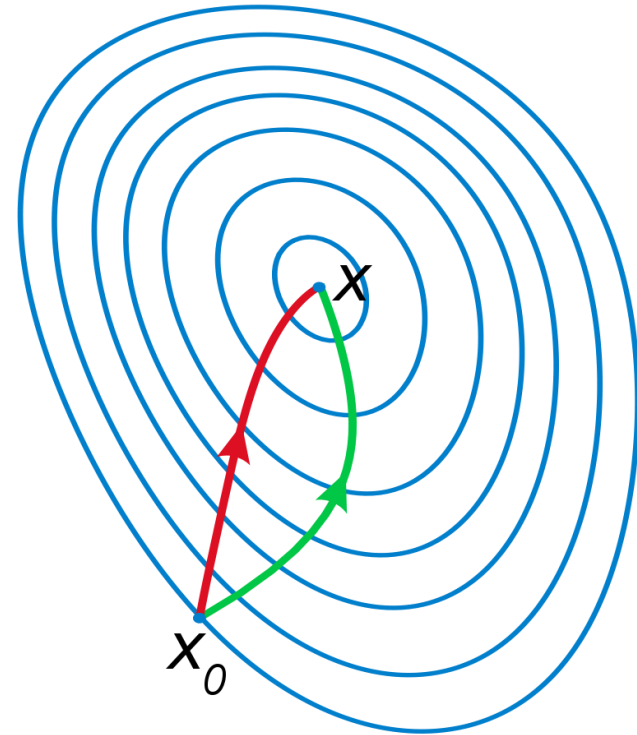
## Solution 2 - Newton-Rhapson:

$$\mathbf{R}_{n+1} = \mathbf{R}_n - \gamma[\mathbf{H}(\mathbf{R}_n)]^{-1} \times \nabla E(\mathbf{R}_n)$$

$$\mathbf{H}(\mathbf{R}_n) = \partial^2 E / \partial \mathbf{R}_n^2$$

## Pros and cons:

Fast convergence to nearest stationary point but requires a cheap (approximate) inverse Hessian



[https://en.wikipedia.org/wiki/Newton%27s\\_method\\_in\\_optimization](https://en.wikipedia.org/wiki/Newton%27s_method_in_optimization)



# The conjugate-gradient algorithm

## Problem:

Follow the forces/stresses to the nearest minimum

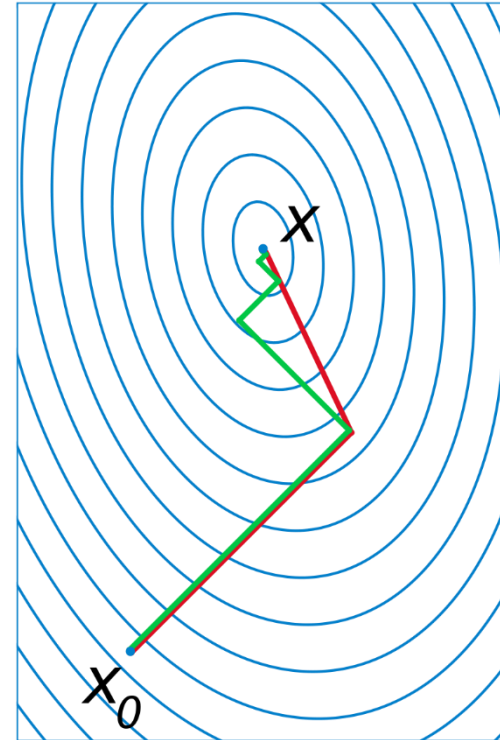
## Solution 3 - Conjugate Gradient:

$$\mathbf{R}_{n+1} = \mathbf{R}_n - k_n \mathbf{h}_n$$

$$\mathbf{h}_n = \frac{\partial E(\mathbf{R}_n)}{\partial \mathbf{R}_n} + \gamma_n \mathbf{h}_{n-1}$$

## Pros and cons:

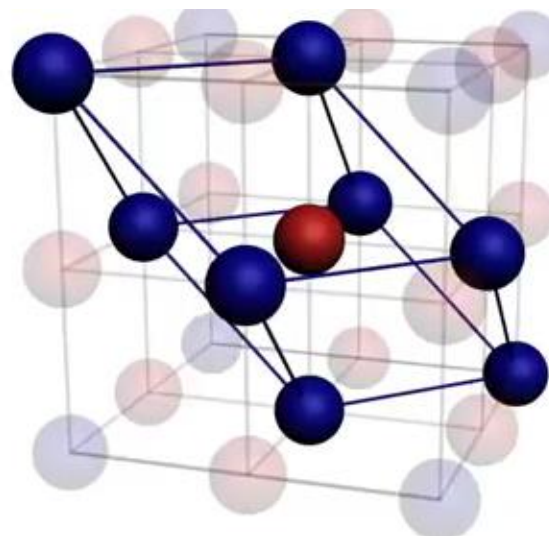
A good middle ground between steepest descent and Newton-Rhapon for convergence speed and cost



[https://en.wikipedia.org/wiki/Gradient\\_descent](https://en.wikipedia.org/wiki/Gradient_descent)

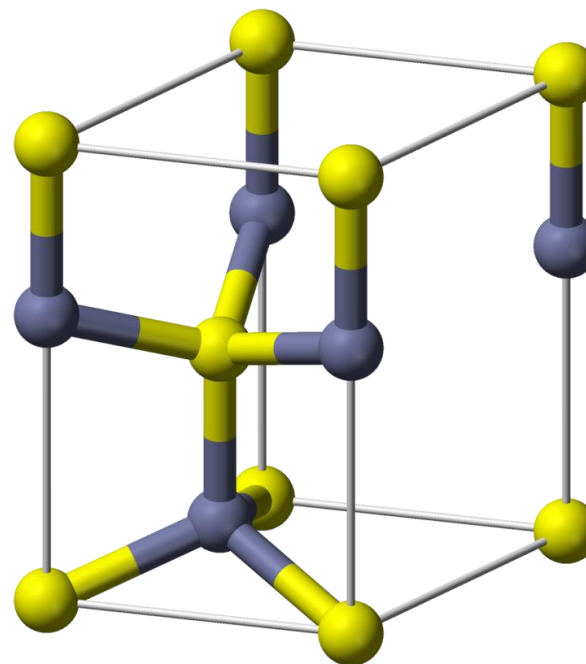
[http://spindynamics.org/documents/cqc\\_lecture\\_6.pdf](http://spindynamics.org/documents/cqc_lecture_6.pdf)

- Crystal symmetry can significantly reduce the number of degrees of freedom
- NaCl ( $Fm\bar{3}m$ ):
  - Atoms fixed at  $(0, 0, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
  - $a = b = c$  and  $\alpha = \beta = \gamma = 90$
  - One DoF: the lattice constant  $a$



Physics-Animations.com: <https://www.youtube.com/watch?v=lmQlxbU9CEI>

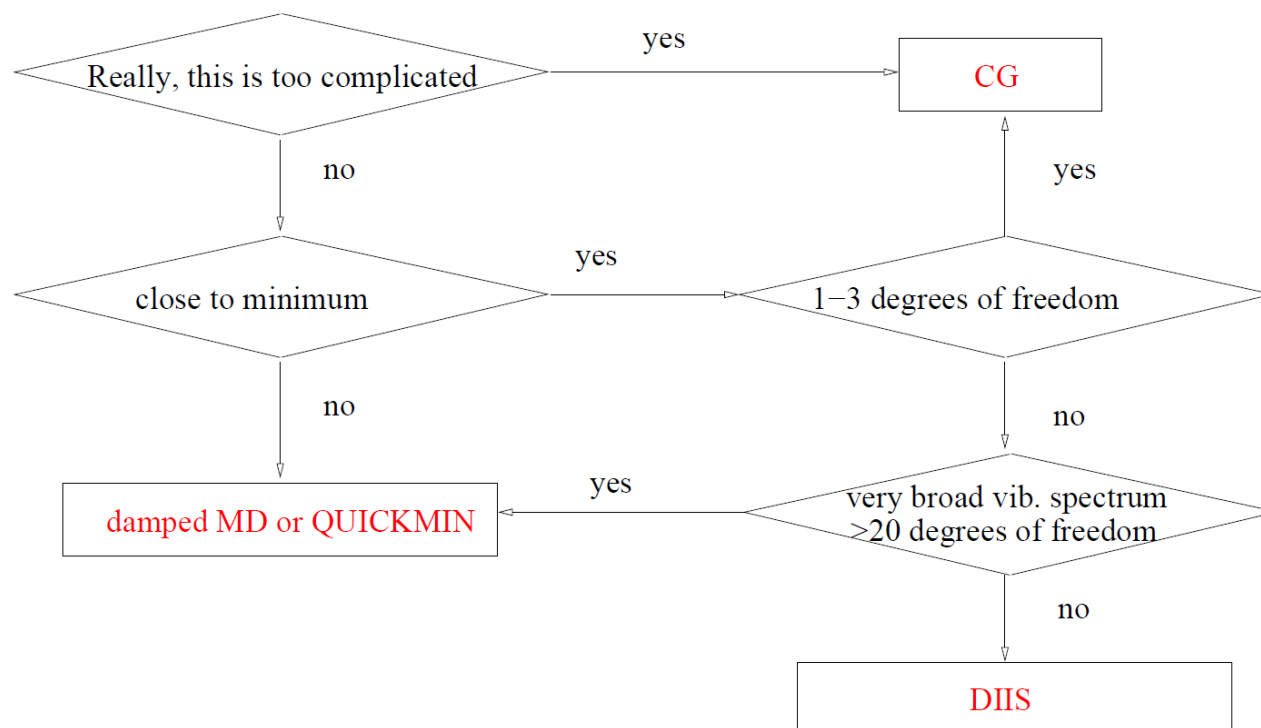
- Crystal symmetry can significantly reduce the number of degrees of freedom
- Wurtzite ZnO ( $P6_3mc$ ):
  - Atoms at  $(0, 0, 0)$  and  $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$
  - $a = b \neq c$ ,  $\alpha = \beta = 90$  and  $\gamma = 120$
  - Three DoFs:  $a$ ,  $c$  and  $u$



<https://en.wikipedia.org/wiki/Wurtzite#/media/File:Wurtzite-unit-cell-3D-balls.png>

- Geometry optimisation is activated by specifying the `IBRION` tag:
  - `IBRION = 0` performs ab initio MD  
(Not strictly geometry optimisation, but a few ps of high-temperature MD can help with structures that are trapped in a local minimum.)
  - `IBRION = 1` relaxes the ions and/or cell using a Quasi-Newtonian algorithm  
(Useful for geometries that are close to a minimum.)
  - `IBRION = 2` relaxes using the conjugate gradient algorithm  
(Good general choice, particularly for initial geometries that are away from a minimum.)
  - `IBRION = 3` relaxes with damped MD or the steepest-descent algorithm  
(I have never used this so I have no experience with it...)

<https://cms.mpi.univie.ac.at/wiki/index.php/IBRION>



[https://www.vasp.at/vasp-workshop/lectures/VASP\\_lecture\\_Basics3.pdf](https://www.vasp.at/vasp-workshop/lectures/VASP_lecture_Basics3.pdf)

- The `ISIF` tag sets the details of what to optimise - choose between different combinations of the atom positions, the cell shape and the cell volume:

	Pos.	Shape	Vol.
<code>ISIF = 2</code>	✓	✗	✗
<code>ISIF = 3</code>	✓	✓	✓
<code>ISIF = 4</code>	✓	✓	✗
<code>ISIF = 5</code>	✗	✓	✗
<code>ISIF = 6</code>	✗	✓	✓
<code>ISIF = 7</code>	✗	✗	✓

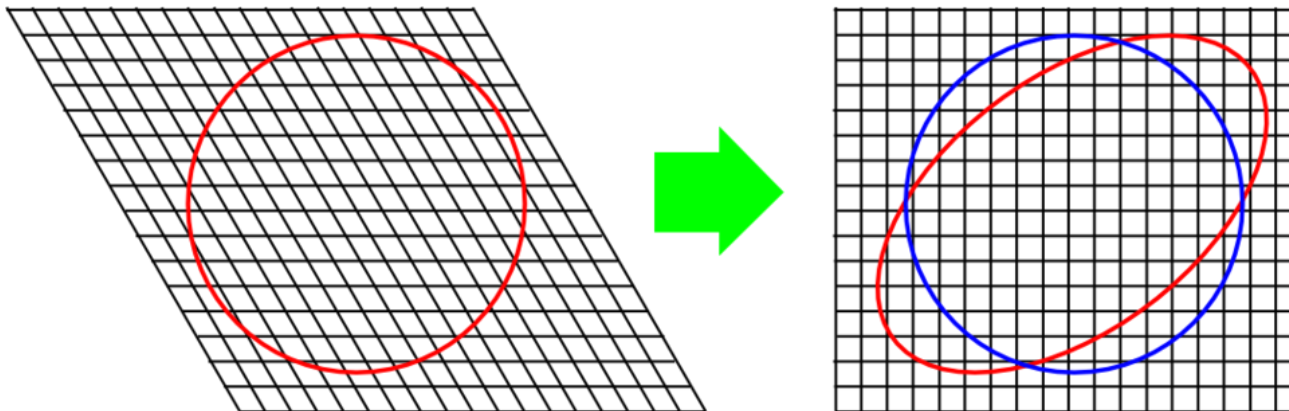
<https://cms.mpi.univie.ac.at/wiki/index.php/ISIF>

- The break criterion for the optimisation loop is set by the EDIFFG tag:
  - $\text{EDIFFG} > 0$ : break when change in energy between successive ionic steps falls below  $E_0(N) - E_0(N - 1) < \text{EDIFFG}$
  - $\text{EDIFF} = 0$ : no break criterion - run for NSW steps
  - $\text{EDIFFG} < 0$ : break when maximum force  $F_{\text{max}} < |\text{EDIFFG}|$
- The number of steps in the optimisation is controlled by NSW:
  - Should be set to a relatively small value (e.g.  $\text{NSW} = 10-25$ ) for  $\text{ISIF} > 2$
- POTIM controls how far the atoms move between ionic steps:
  - For relaxations ( $\text{IBRION} = 1-3$ ), specifies a scaling constant (default:  $\text{POTIM} = 0.5$ )
  - For MD simulations ( $\text{IBRION} = 0$ ), POTIM sets the MD timestep (no default - must be specified)

- `ISYM` can be used to control symmetry handling
  - For optimisations, usually helpful to leave `ISYM = 2/3` (on - default)
  - For MD simulations, almost certainly want to set `ISYM = 0` (off)



- The plane-wave basis depends on the reciprocal lattice vectors and hence the cell shape/volume: during a variable-cell optimisation the basis set becomes incomplete and leads to artificial Pulay forces



- To mitigate this:
  - Increase `ENCUT` to  $1.3-2 \times \text{max(ENMAX)}$  in the `POTCAR` files
  - Perform variable-cell optimisations as a series of shorter steps (`NSW` = 10–25)

[https://howlingpixel.com/i-en/Pulay\\_stress](https://howlingpixel.com/i-en/Pulay_stress)

- Most of the examples include job files and Python scripts to automate some tasks:
  - `Opt.py`

Repeats a VASP calculation until a run completes in  $N < N_{SW}$  steps - useful for variable-cell optimisations
  - `Opt-EV.py`

Performs a series of geometry optimisations, as in `Opt.py`, starting from a POSCAR file and scaling the volume, and outputs an  $E/V$  curve.
  - `ModeMap.py`

Reads phonon eigenvectors from an OUTCAR file, sets up and runs a series of single-point energy calculations on displacements of a reference POSCAR along a selected mode, and generates a mode PES
- If you find these useful, feel free to take them and adapt them to your own materials.
- (Disclaimer: The Python scripts should work for the workshop examples - I hope! - but they are not “bulletproof”, so check they will work for what you need to do and note any warnings in the files.)

# Example #1: $\text{Cu}_2\text{ZnSnS}_4$ (CZTS)

```
! Technical.
```

```
ENCUT = 600
```

```
GGA = PS
```

```
LASPH = .TRUE.
```

```
LREAL = .FALSE.
```

```
PREC = Accurate
```

```
! Electronic SCF.
```

```
ALGO = Normal
```

```
EDIFF = 1e-8
```

```
ISMEAR = 0
```

```
SIGMA = 0.01
```

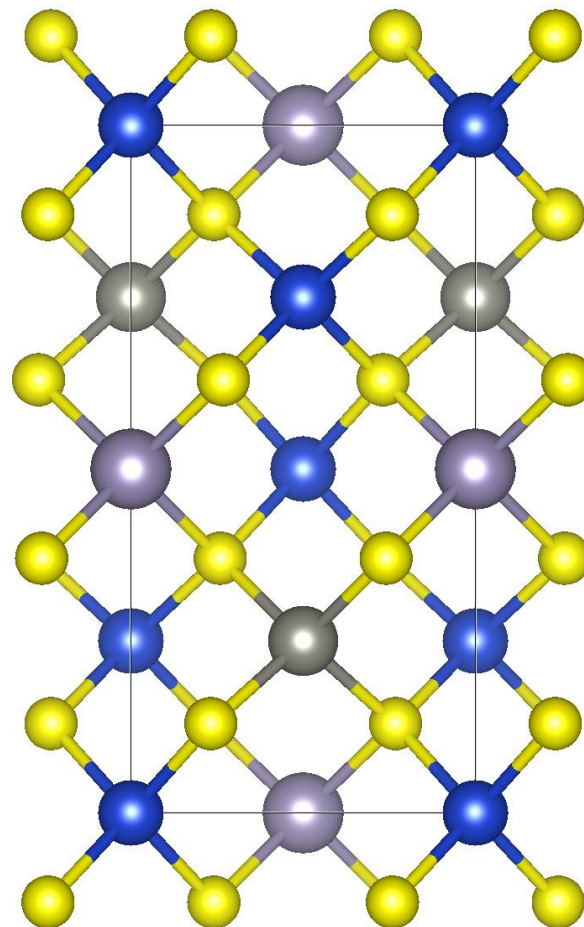
```
! Geometry optimisation.
```

```
EDIFFG = -1e-2
```

```
IBRION = 1
```

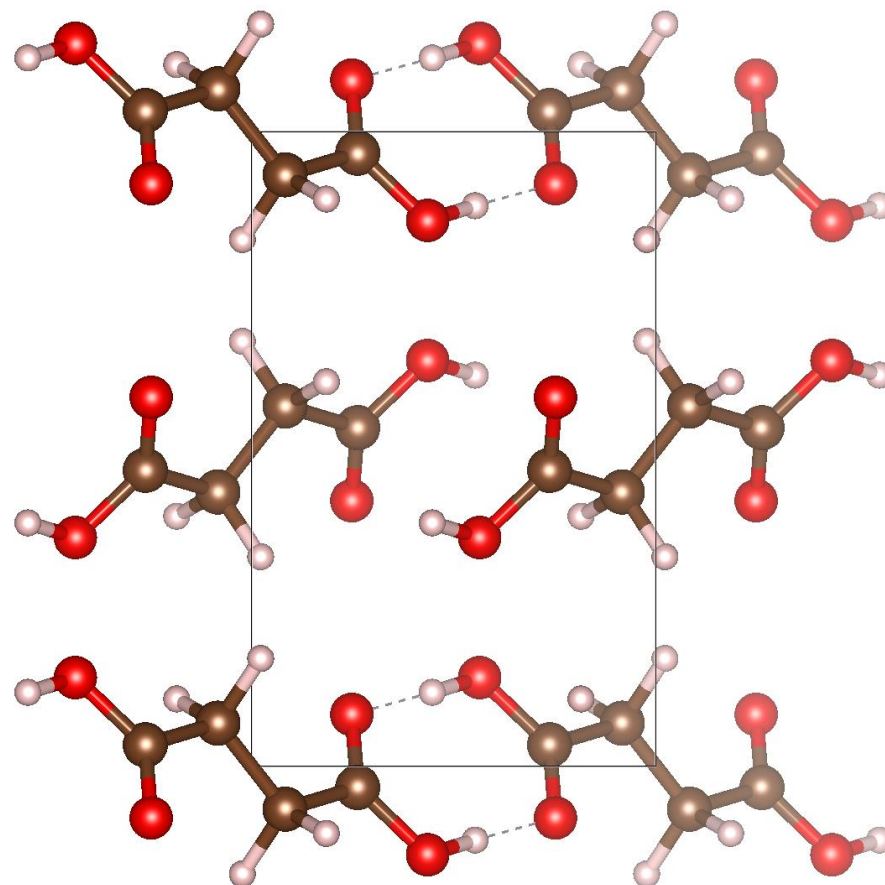
```
ISIF = 3
```

```
NSW = 25
```



# Example #2: $\beta$ -succinic acid

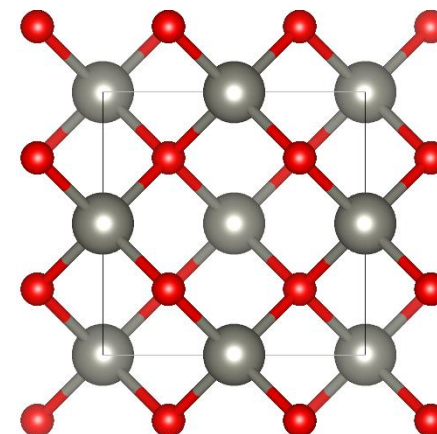
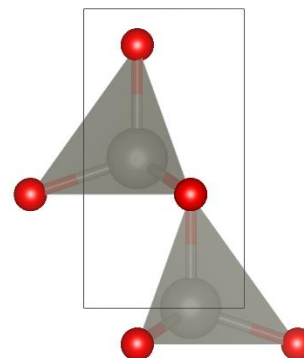
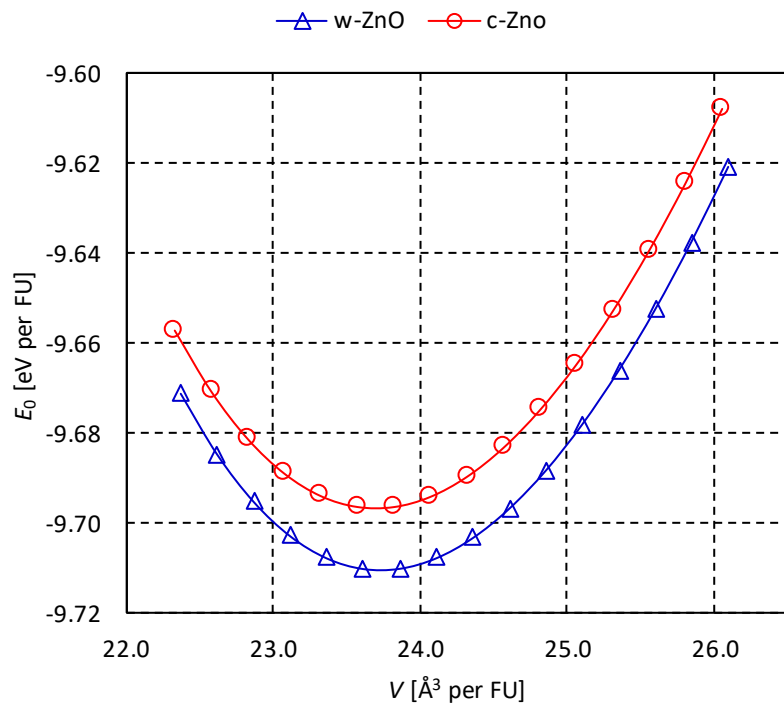
```
! Technical.  
  
ENCUT = 800  
GGA = PE  
IVDW = 11  
LASPH = .TRUE.  
LREAL = .FALSE.  
PREC = Accurate  
  
! Electronic SCF.  
  
ALGO = Normal  
EDIFF = 1e-8  
ISMEAR = 0  
SIGMA = 0.01  
  
! Geometry optimisation.  
  
EDIFFG = -1e-2  
IBRION = 2  
ISIF = 4  
NSW = 25
```



- An alternative way to obtain the equilibrium volume is to calculate an  $E(V)$  curve:
  - Perform a series of constant-volume relaxations
  - Locate minimum by fitting to an equation of state (EoS) such as Birch-Murnaghan EoS - gives equilibrium volume  $V_0$ , energy  $E_0$  and also bulk modulus  $B_0$ :

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[ \left( \frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B'_0 + \left[ \left( \frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[ 6 - 4 \left( \frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\}$$

# Example #3: *c*-ZnO vs. *w*-ZnO



- The Selective Dynamics keyword in the POSCAR file can be used to freeze atomic positions during geometry optimisations (or MD simulations)

```
NaCl <100> (Na -> K)
1.0000000000000000
11.2804000000000002 0.0000000000000000 0.0000000000000000
0.0000000000000000 11.2804000000000002 0.0000000000000000
0.0000000000000000 0.0000000000000000 31.9206000000000003
Na Cl K
47 48 1
Selective Dynamics
Direct
0.0000000000000000 0.0000000000000000 0.2791316579262295 T T T
0.0000000000000000 0.0000000000000000 0.4558263315852459 F F F
0.0000000000000000 0.0000000000000000 0.6325210052442624 T T T
0.0000000000000000 0.2500000000000000 0.3674789947557377 T T T
0.0000000000000000 0.2500000000000000 0.5441736684147541 F F F
0.0000000000000000 0.2500000000000000 0.7208683420737706 T T T
0.0000000000000000 0.4999999999999999 0.2791316579262295 T T T
0.0000000000000000 0.4999999999999999 0.4558263315852459 F F F
0.0000000000000000 0.4999999999999999 0.6325210052442624 T T T
0.0000000000000000 0.7500000000000000 0.3674789947557377 T T T
0.0000000000000000 0.7500000000000000 0.5441736684147541 F F F
```

# Example #4: NaCl <100> with K defect

NaCl <100> (Na -> K)

1.0000000000000000

11.2804000000000002

0.0000000000000000

0.0000000000000000

0.0000000000000000

11.2804000000000002

0.0000000000000000

0.0000000000000000

0.0000000000000000

31.9206000000000003

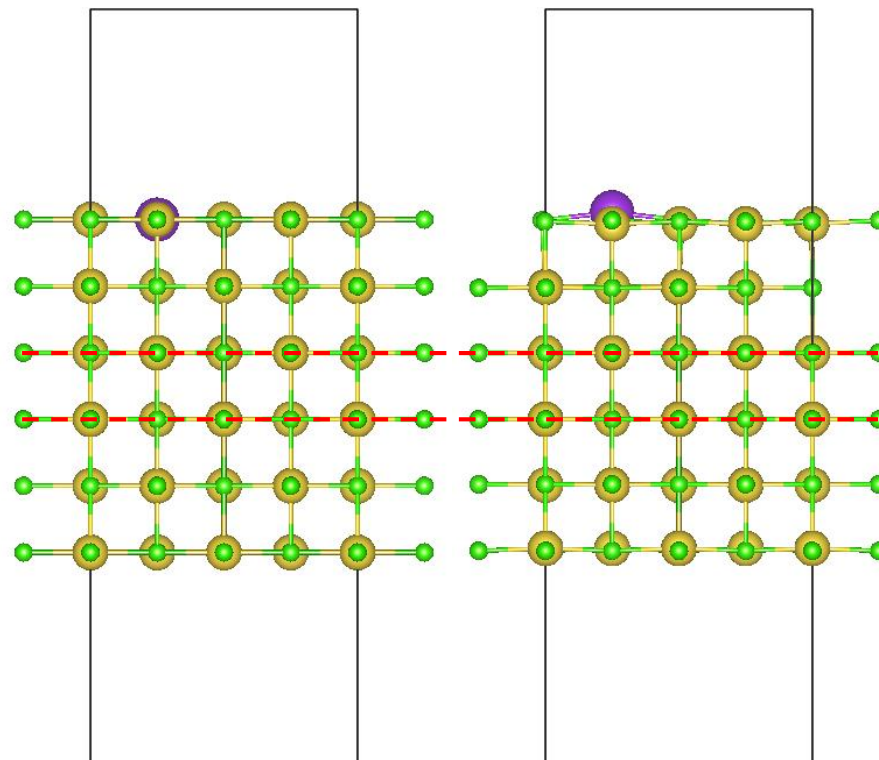
Na Cl K

47 48 1

Selective Dynamics

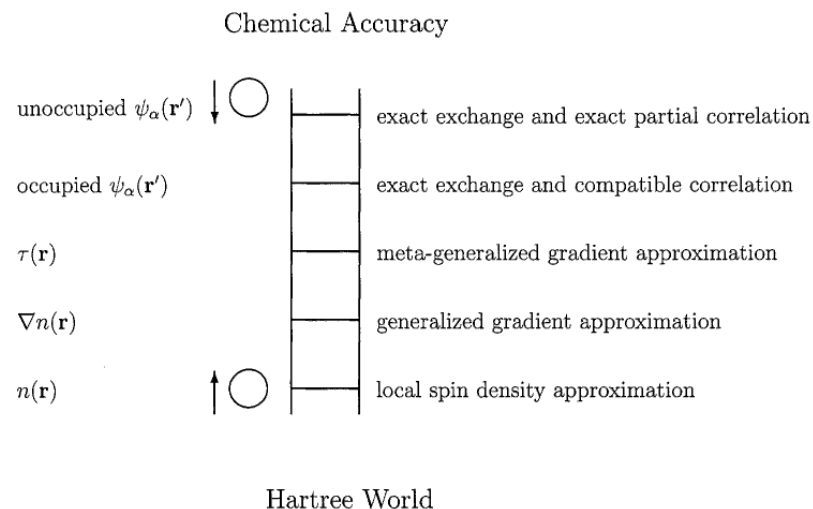
Direct

0.00000...	0.00000...	0.27913...	T	T	T
0.00000...	0.00000...	0.45582...	F	F	F
0.00000...	0.00000...	0.63252...	T	T	T
0.00000...	0.25000...	0.36747...	T	T	T
0.00000...	0.25000...	0.54417...	F	F	F
0.00000...	0.25000...	0.72086...	T	T	T
0.00000...	0.49999...	0.27913...	T	T	T
0.00000...	0.49999...	0.45582...	F	F	F
0.00000...	0.49999...	0.63252...	T	T	T
0.00000...	0.75000...	0.36747...	T	T	T
0.00000...	0.75000...	0.54417...	F	F	F
0.00000...	0.75000...	0.72086...	T	T	T
0.25000...	0.00000...	0.36747...	T	T	T
0.25000...	0.00000...	0.54417...	F	F	F
0.25000...	0.00000...	0.72086...	T	T	T
0.25000...	0.25000...	0.27913...	T	T	T
0.25000...	0.25000...	0.45582...	F	F	F
0.25000...	0.25000...	0.63252...	T	T	T
0.25000...	0.49999...	0.36747...	T	T	T
0.25000...	0.49999...	0.54417...	F	F	F
0.25000...	0.49999...	0.72086...	T	T	T
0.25000...	0.75000...	0.27913...	T	T	T
0.25000...	0.75000...	0.45582...	F	F	F
0.25000...	0.75000...	0.63252...	T	T	T
0.49999...	0.00000...	0.27913...	T	T	T
0.49999...	0.00000...	0.45582...	F	F	F
0.49999...	0.00000...	0.63252...	T	T	T





- Provided other technical parameters - ENCUT, KPOINTS, PREC - are converged, the choice of XC functional is the most important factor for getting good results
- Although LDA and PBE are very widely used in the literature, they are not always the best for geometry optimisation (!)
- It is fairly common practice to optimise the geometry with one XC functional and model the electronic structure with another (e.g. PBEsol  $\rightarrow$  HSE 06)

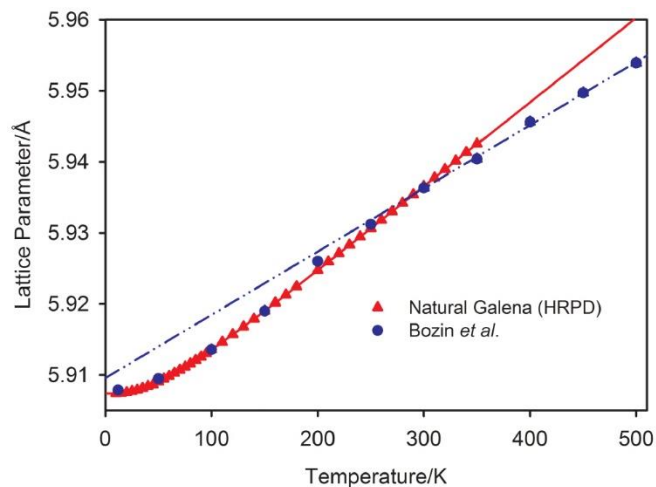


**FIGURE 1.** Jacob's ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational resources. However, at present their safety can be guaranteed only on the two lowest rungs.

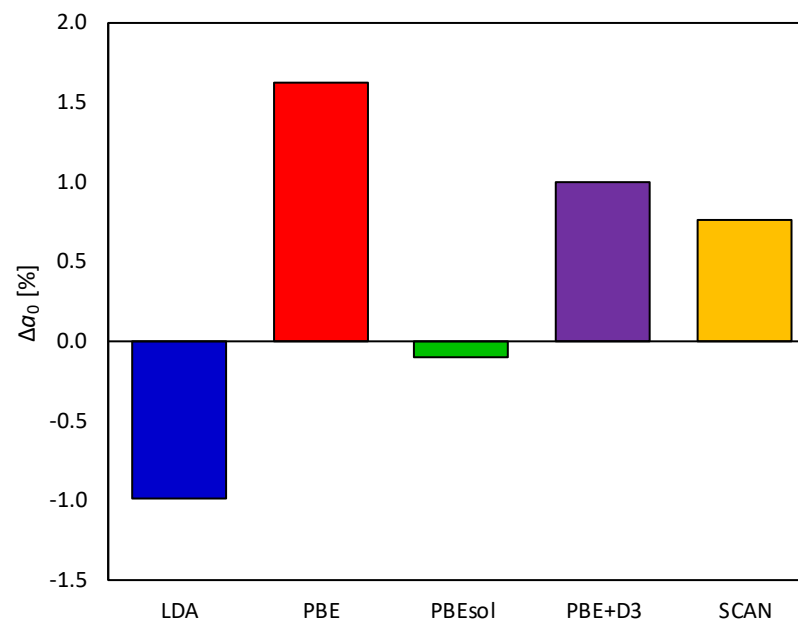
Perdew and Schmidt, *AIP Conf. Proc.* **577**, 1 (2001), DOI: [10.1063/1.1390175](https://doi.org/10.1063/1.1390175)

- LDA:
  - Selected automatically when using POTCAR files from the `potpaw_LDA.*` set
- PBE (standard GGA):
  - Set `GGA = PE` or use the `potpaw_PBE.*` set.
- PBEsol (improved GGA for solids):
  - Set `GGA = PS`
- PBE + D3 (PBE GGA with the D3 dispersion correction):
  - Add `IVDW = 11` to a PBE calculation
- SCAN (modern meta-GGA):
  - Add `METAGGA = SCAN` to a PBE calculation
  - Usually best to use `ALGO = Normal` and `LMIXTAU = .TRUE.`

# Example #5: PbS



$$a(T) = a_0 + k \frac{1}{[\exp(E/T) - 1]}$$



Knight, *J. Phys.: Condens. Matter* **26**, 385403 (2014), DOI: [10.1088/0953-8984/26/38/385403](https://doi.org/10.1088/0953-8984/26/38/385403)

## 1. Obtain a good starting structure:

- Preferably choose a high-quality single-crystal X-ray or neutron structure collected at low  $T$
- Be careful with structures containing disorder/partial occupancies
- The Materials Project website (<https://materialsproject.org>) is a good alternative to the ICSD for downloading initial structures

## 2. Choose a good XC functional:

- Hard bulk materials (e.g. oxides): try PBEsol (GGA = PS)
- Layered or molecular materials: try PBE + D3 (GGA = PE with IVDW = 11)

## 3. Choose your ISIF:

- ISIF = 2: internal coordinates (atom positions) only
- ISIF = 4: cell shape with fixed volume
- ISIF = 3: full variable-cell optimisation

4. Adjust your `ENCUT` if required:

- $1.3-2 \times \max(\text{ENMAX})$  for accurate forces and stresses - especially important for variable-cell optimisations

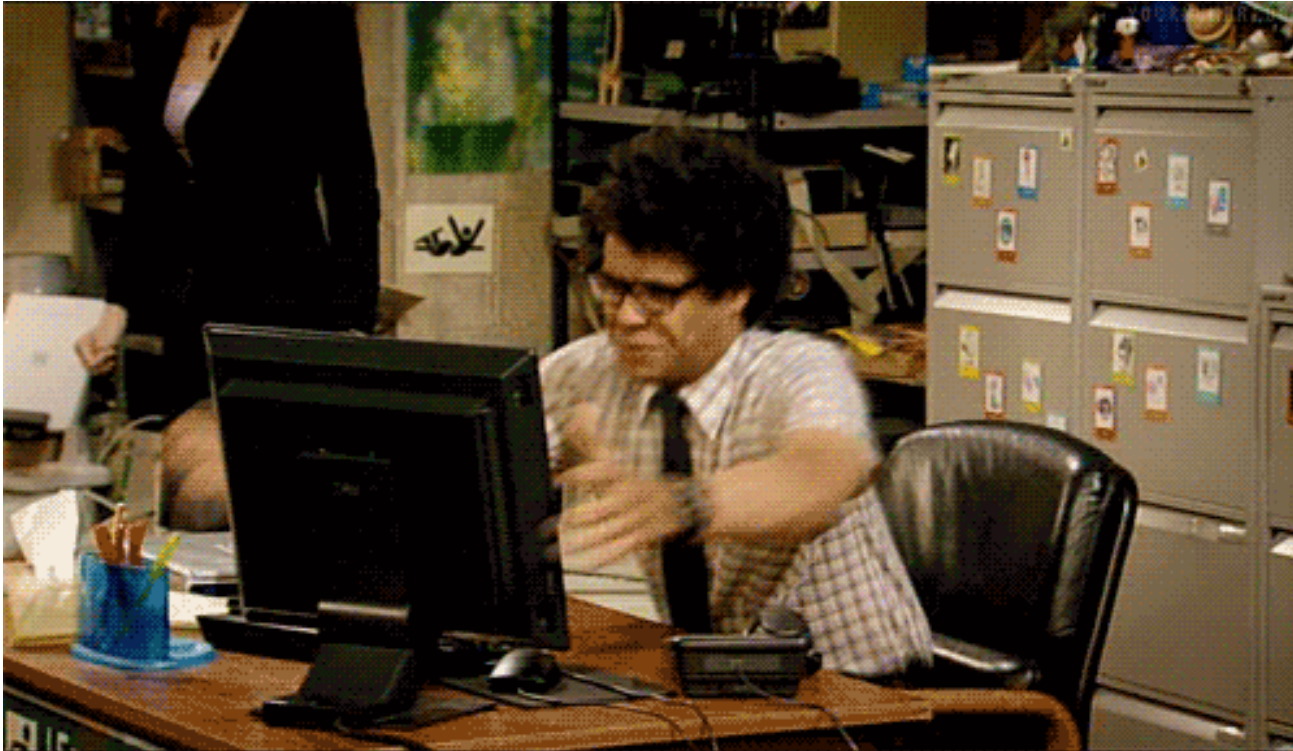
5. Choose your `IBRION`:

- Start with `IBRION = 2` and change to `IBRION = 1` as the ionic energy begins to converge

6. Make sure your electronic structure is well converged:

- If the electronic SCF fails to converge, the forces will probably not be accurate -> try `ALGO = Normal/All` and increase `NELM` if required
- If using a loose `EDIFF`, the forces might not be accurate enough to converge to a tight `EDIFFG` (e.g. `EDIFF = 1e-4` with `EDIFFG = -1e-2`)
- A failed SCF step in the middle of an optimisation could easily undo several prior successful minimisation steps

# What to do when things go wrong?



Source: MovieGif.com via <http://gph.is/1xzJdX3>

## Problem:

My optimisation is taking a long time to converge.

## Things to check:

1. Are your electronic SCF steps converging consistently? One failed SCF can undo several optimisation steps.
2. Is your `EDIFFG` sane? Reaching `EDIFFG = -1e-3` in a large, low-symmetry structure is hard, and rarely actually necessary.
3. Are your `EDIFF` and `EDIFFG` compatible? (See summary slides.)

## Things to try:

1. Change `IBRION` (`IBRION = 1/2`).
2. For systems with H atoms or a relatively flat PES, try `POTIM = 0.25`).

## Problem:

My optimisation is diverging.

## Things to check:

1. Are your electronic SCF steps converging?
2. Is your input structure reasonable? (Experimental structures are definitely *not* infallible - check for guesstimated H positions, partial occupancies, and dodgy CIF files.)
3. Is your POTCAR file ordered correctly?
4. If using spin polarisation, are your MAGMOM/NUPDOWN set correctly?

## Things to try:

1. Start with `ISIF = 2` to constrain volume/shape and/or do a few ionic steps with a very small `POTIM` (e.g. `POTIM = 0.05`) to constrain initial explosion.



## Problem:

My optimised structure doesn't match experiment/previous calculations.

## Things to check:

### 1. If comparing to experiment:

- Is the experimental structure good quality?
- Have you considered thermal expansion?
- Ideally want single-crystal X-ray or neutron data recorded close to 0 K.

### 2. If comparing to other calculations:

- Are you using a comparable setup? (XC functional, cutoff,  $k$ -point sampling, ...)
- Are your chosen parameters more appropriate than those used in previous work?

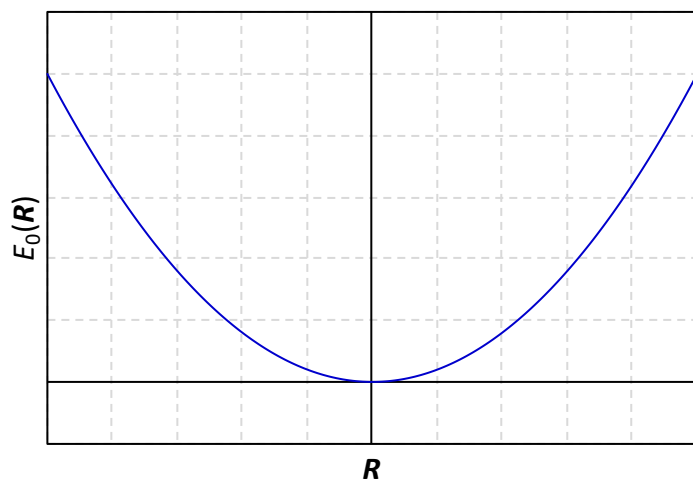
## Things to try:

1. Try different XC functionals - PBEsol or PBE-D3 instead of PBE.

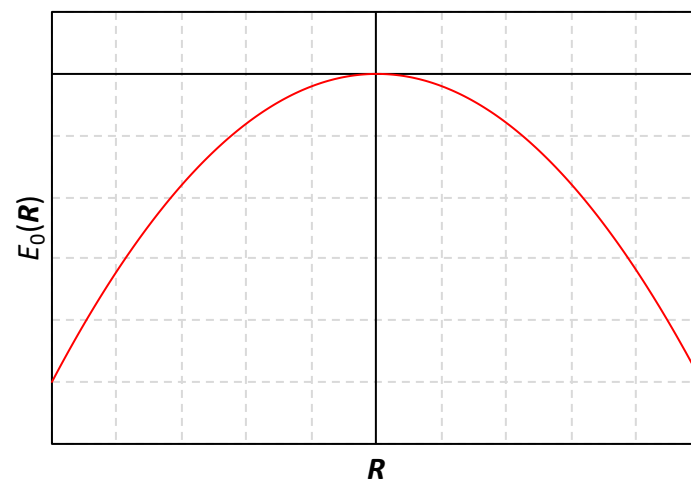
# Not all stationary points are equal...

## Problem:

Find the set of atomic positions  $\mathbf{R} = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$  and lattice vectors  $\mathbf{a} = \{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$  that define the minimum (a **stationary point**) on the potential-energy surface.



Minimum:  $\frac{\partial^2 E}{\partial R^2} > 0$

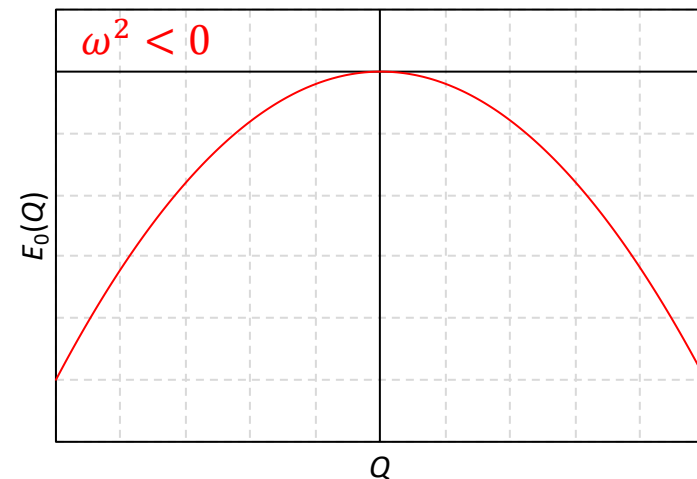
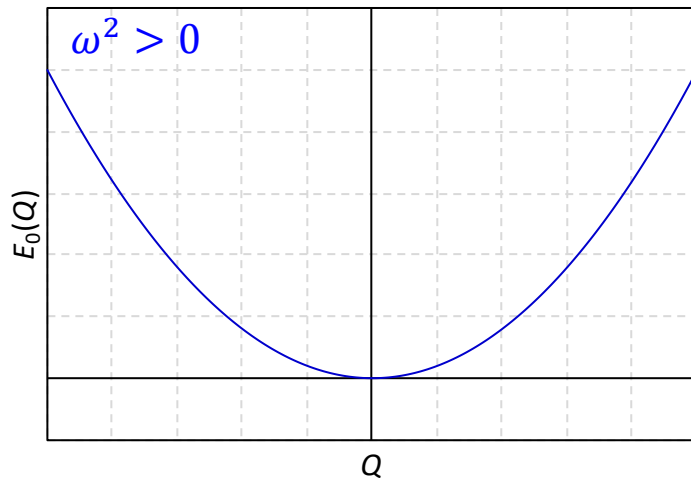


Maximum:  $\frac{\partial^2 E}{\partial R^2} < 0$

## Solution:

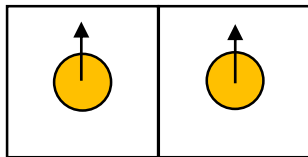
Computing the force constants  $\Phi = \partial^2 E / \partial \mathbf{R}^2$  and obtaining the harmonic phonon frequencies from the dynamical matrix  $\mathbf{D}(\mathbf{q})$  allows us to confirm we have located a minimum

$$D_{\alpha\beta}(jj', \mathbf{q}) = \frac{1}{\sqrt{m_j m_{j'}}} \sum_{l'} \Phi_{\alpha\beta}(j0, j'l') \exp[i\mathbf{q} \cdot \{\mathbf{r}(j'l') - \mathbf{r}(j'l')\}]$$

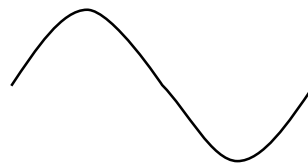
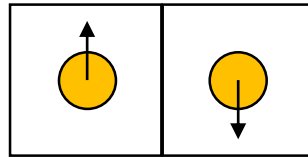


- Phonon calculations are activated by setting `IBRION = 5-8`:
  - `IBRION = 5/6`: calculate force constants and determine  $\mathbf{D}(\mathbf{q} = \Gamma)$  using finite differences
  - `IBRION = 7/8`: evaluate  $\mathbf{D}(\mathbf{q} = \Gamma)$  using DFPT (not available for all functionals)
  - `IBRION = 6/8` take into account symmetry, whereas `IBRION = 5/7` do not
- For finite differences calculations (`IBRION = 5/6`):
  - `POTIM` sets the finite difference step (default:  $1.5 \times 10^{-2}$  Å)
  - `NFREE` sets the number of steps in the central difference scheme (default: 2)
- For at least some versions of VASP it is also necessary to specify `NSW = 1`
- In a finite-differences calculation (`IBRION = 5/6`), adding `ISIF = 3` determines the elastic constant matrix and the ionic contribution to the dielectric constant  $\epsilon$
- In either calculation, Born charges and the polarisation contribution to  $\epsilon$  can be obtained using `LEPSILON` (DFPT) or `LCALCEPS` (finite field)

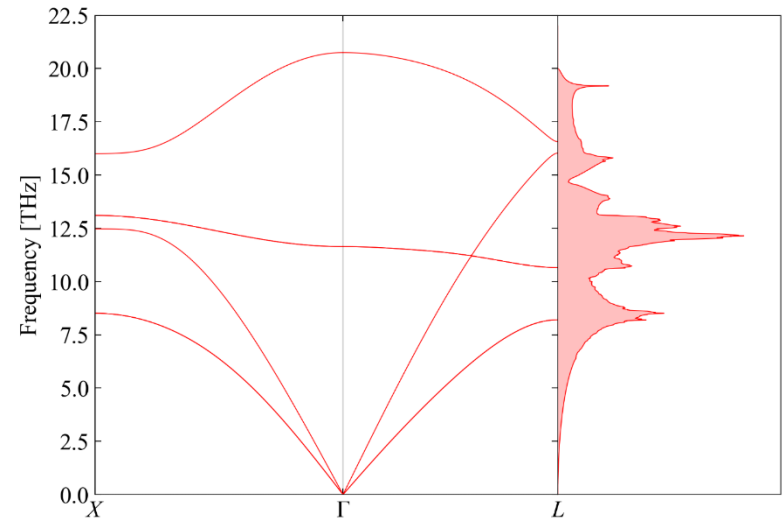
- The major drawback is that at present the VASP routines only calculate  $\mathbf{D}(\mathbf{q} = \Gamma)$ ...
- ... but the Phonopy package provides a full set of functionality and works very well with VASP as a force calculator: <https://atztogo.github.io/phonopy/>



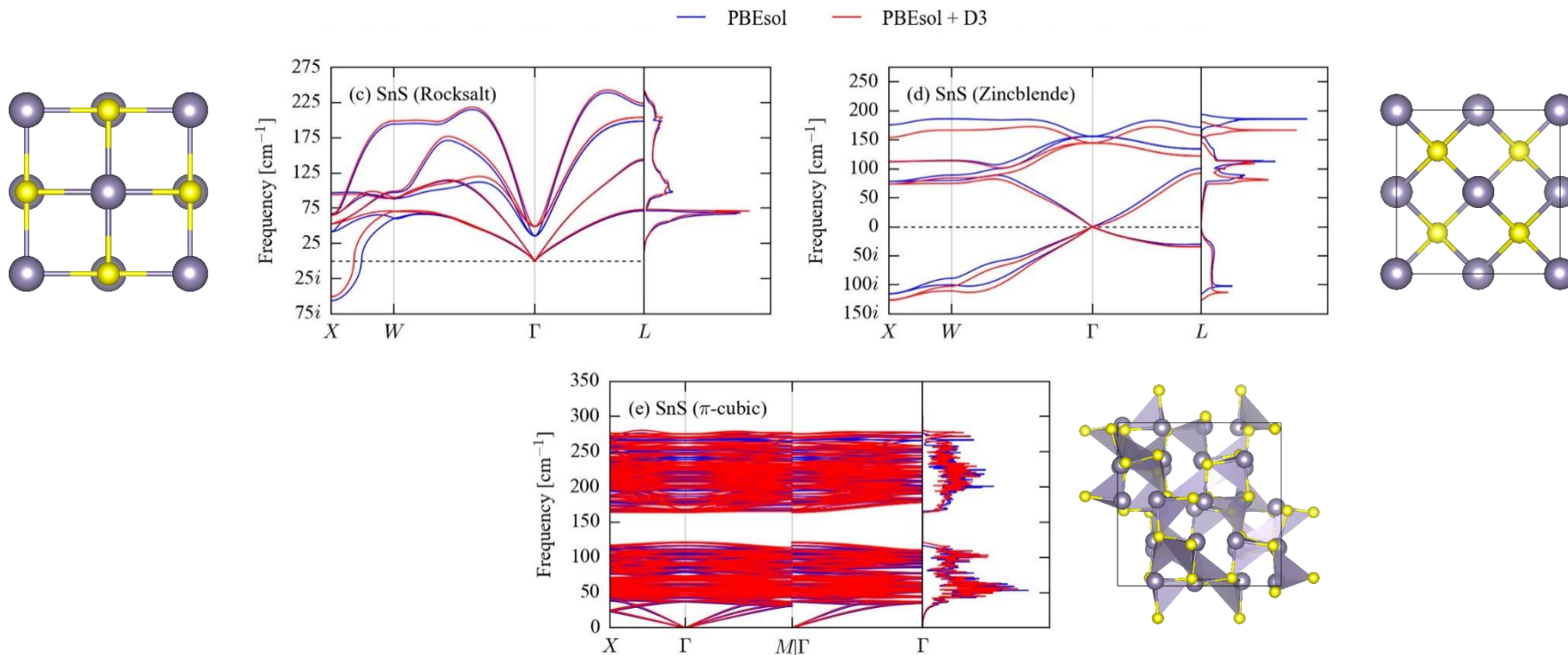
Zone centre ( $\Gamma$ )



Zone boundary



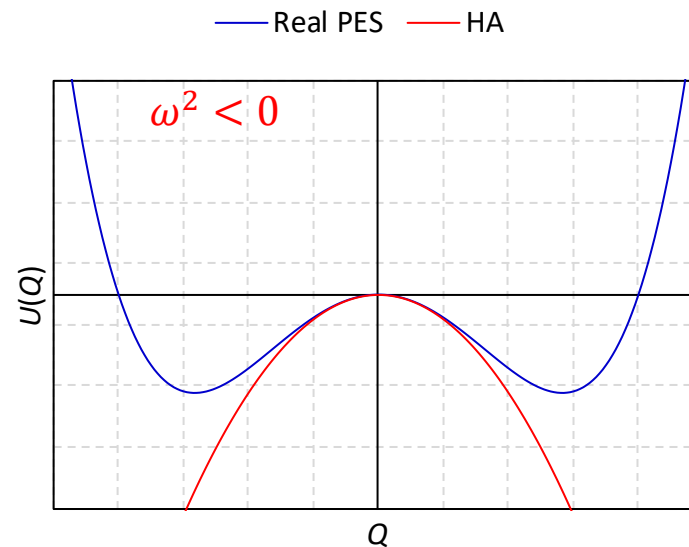
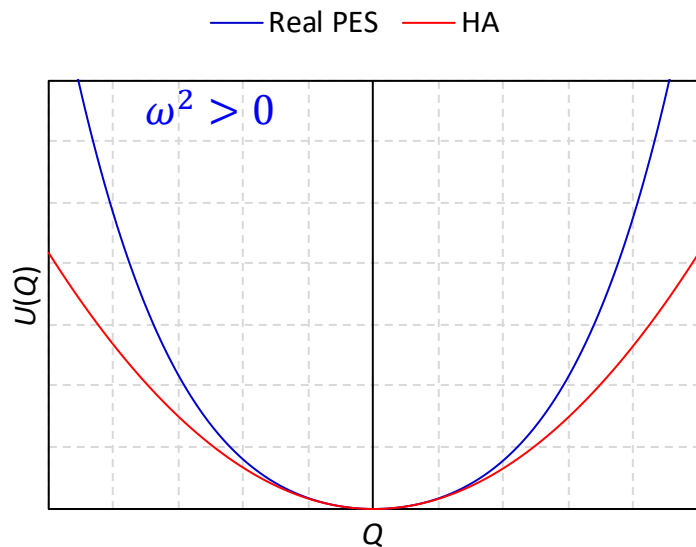
# Structural instabilities: “cubic” SnS



Skelton *et al.*, *J. Phys. Chem. C* **121** (12), 6446 (2017), DOI: [10.1021/acs.jpcc.6b12581](https://doi.org/10.1021/acs.jpcc.6b12581)

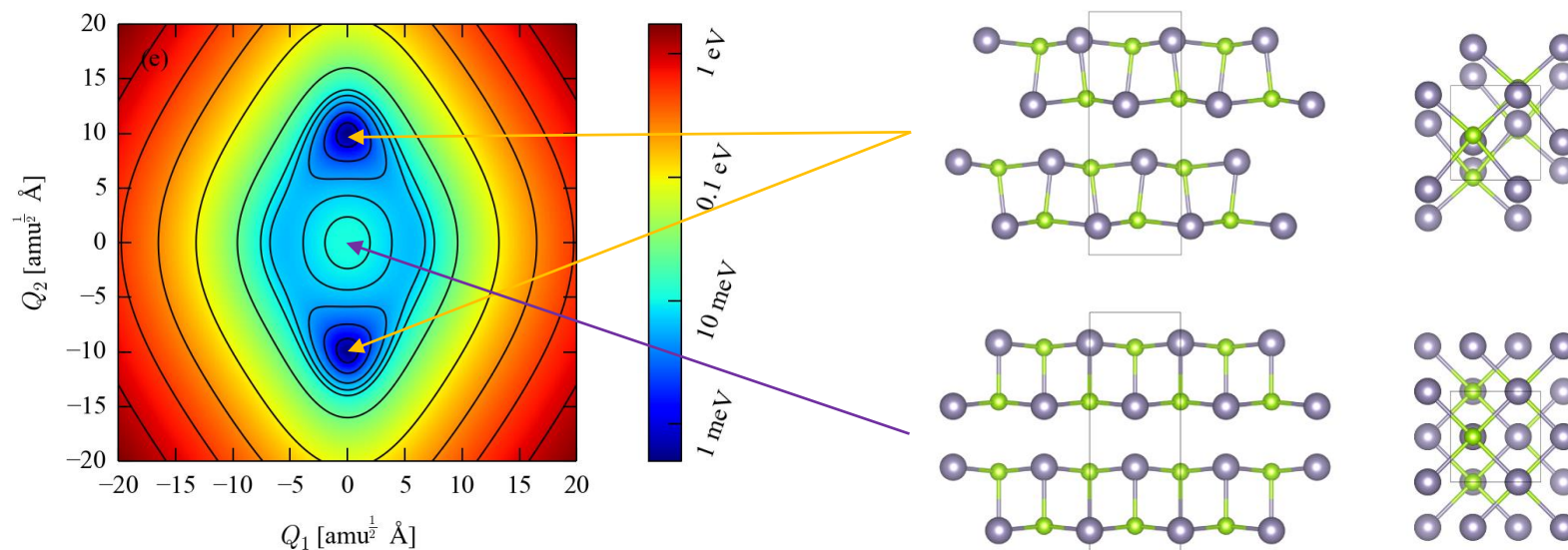
# Are imaginary modes always bad?

- In some systems, equivalent energetic minima are separated by a shallow energy barriers - at high temperatures, sufficient thermal energy is available to hop between minima on a short timescale, and crystallography measures the average structure



# Are imaginary modes always bad?

- Many examples of this phenomenon in real materials:
  - Octahedral rotation and cation off-centering in cubic perovskites
  - $Pnma \leftrightarrow Cmcm$  phase transition in SnS/SnSe
  - The paraelectric  $\leftrightarrow$  ferroelectric phase transition in ferroelectrics

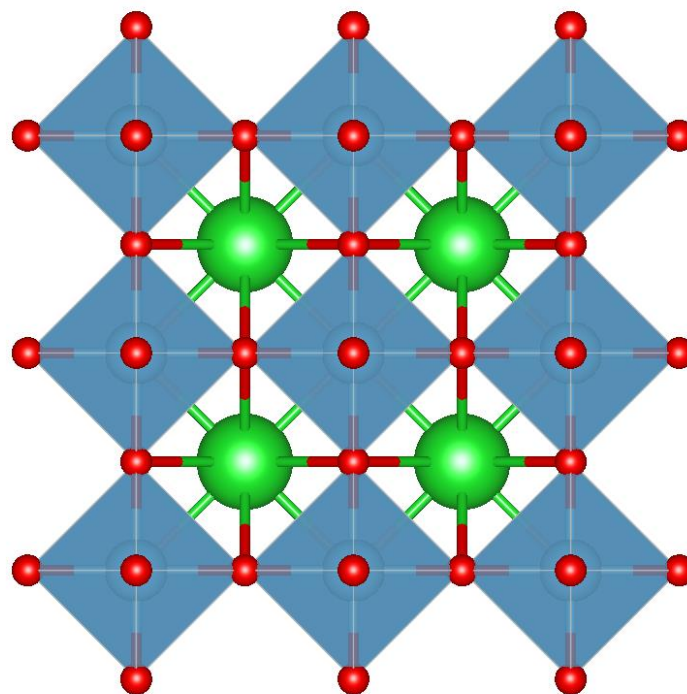
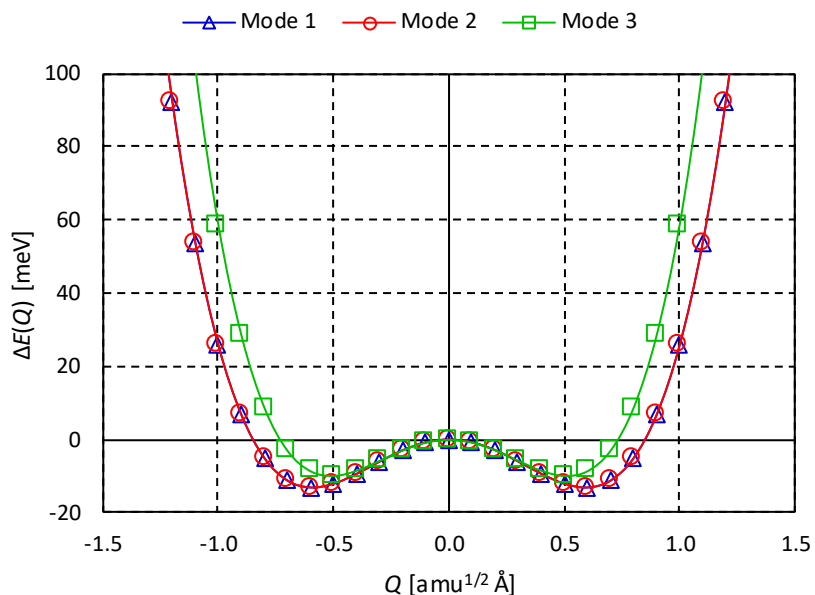


Skelton *et al.*, *Phys. Rev. Lett.* **117**, 075502 (2016), DOI: [10.1103/PhysRevLett.117.075502](https://doi.org/10.1103/PhysRevLett.117.075502)



# Example #6: Cubic BaTiO<sub>3</sub>

- *c*-BaTiO<sub>3</sub> displays a spontaneous off-centring of the Ti<sup>4+</sup> cation within the TiO<sub>6</sub> octahedral cage - manifests as a triply-degenerate imaginary mode with  $\nu \approx 200i$  cm<sup>-1</sup>



Thankyou for listening!

Any questions?