

things-to-do

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1 Tasks

1.1 TODO Has anyone investigated the stacking faults of Omega phase?

- Maybe as Omega phase doesn't occur that often, perhaps it has not been studied in detail.
- I should look further into this

1.2 TODO Finish doing the gamma surfaces for all planes for pure titanium.

1.2.1 Checking the convergence criteria

- Now checking the convergence criteria.

1. How the lattice parameters change with the fineness of the k mesh

- Maybe with a less fine k mesh the lattice parameters become worse.
- SOLUTION: The lattice parameters do not change that much under

differences with the k mesh. File with change of the lattice parameters with k mesh. a vs nk c_{vsnk} e_{vsnk}

(a) What if r_{maxh} is smaller or larger?

- If r_{maxh} is smaller (say $r_{maxh} = 6.7$ bohr) then we get the same results.

Variation of total energy of hcp at minimum lattice parameters with nk

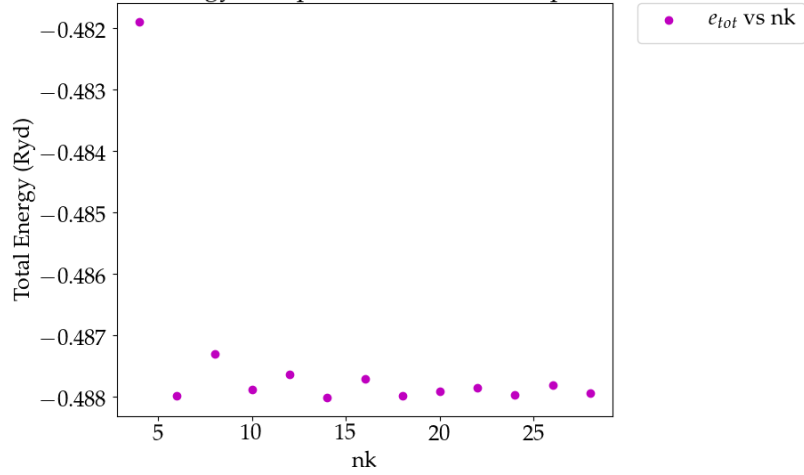


Figure 1: Variation of energy with k mesh.

]]

- Data: a_{hcp} small r_{maxh} , c_{hcp} small r_{maxh} , e_{hcp} small r_{maxh} .

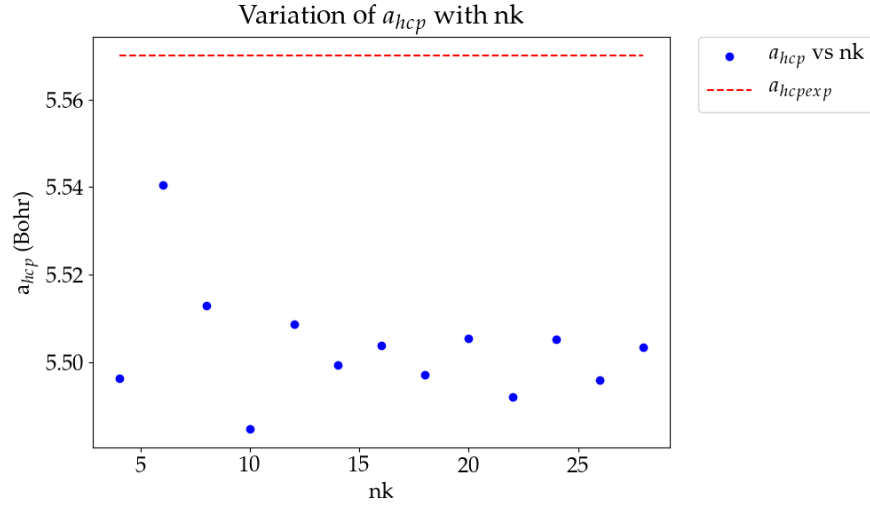


Figure 2: Variation of a hcp with k mesh.

- If rmaxh is larger (rmaxh = 20 bohr), all possible interactions must be included then. And so we get the same results.
 - Data: a_{hcp} large rmaxh, c_{hcp} large rmaxh, e_{hcp} large rmaxh
2. How does rmaxh change the lattice parameters?
- (a) How does rmaxh change the energy of a supercell
- How does the number of neighbours change and what is the relation between rmaxh and larger cell sizes.

1.2.2 Notes on the model.

It seems that there is a lot of charge moving around when doing the relaxations. I think that this may be due to the fact that there is no Hubbard U interactions, a parameter for the coulomb interaction, which stops the charges from moving freely.

- TBE control file is currently set to this:

```
TBE: nbas = 128 nspec = 1 verb 31
TB: rmaxh = 20, m-stat: F-P rlx-vol, rho
bz: metal
```

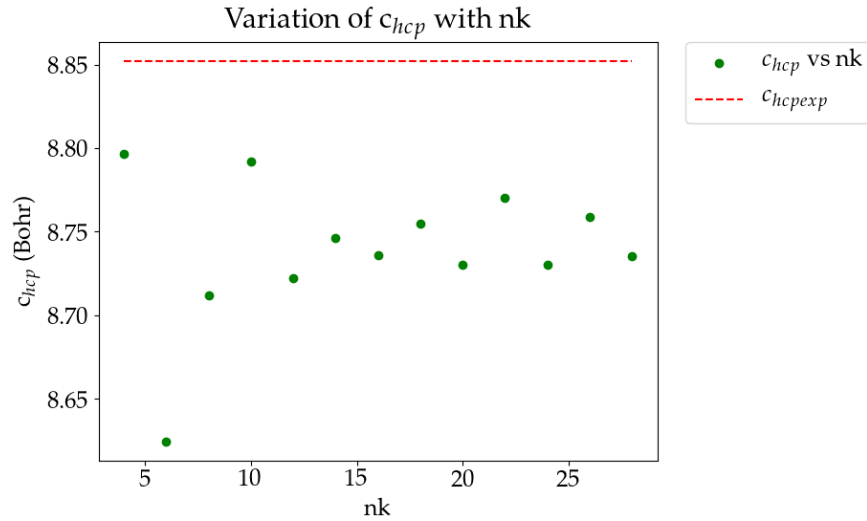


Figure 3: Variation of c_{hcp} with k mesh.

- 1.2.3 **DONE** Implement Homogenous Shear boundary conditions for gamma surface calculation.
- 1.3 **TODO** Python script: remove include statements → One file.
- 1.4 **TODO** Summarise UCL DFT lectures.
- 1.5 **TODO** Write first paragraph of Literature review
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 - 1.5.3 **TODO** Summarise dislocations and Oxygen interactions (review)
- 1.6 **TODO** Write summary of org-mode
- 1.7 **DONE** Investigate why rmaxh changes energy
 - Variation of rmaxh does not change the energy
 - Obviously the number of neighbours changes with rmaxh.

of total energy of hcp at minimum lattice parame

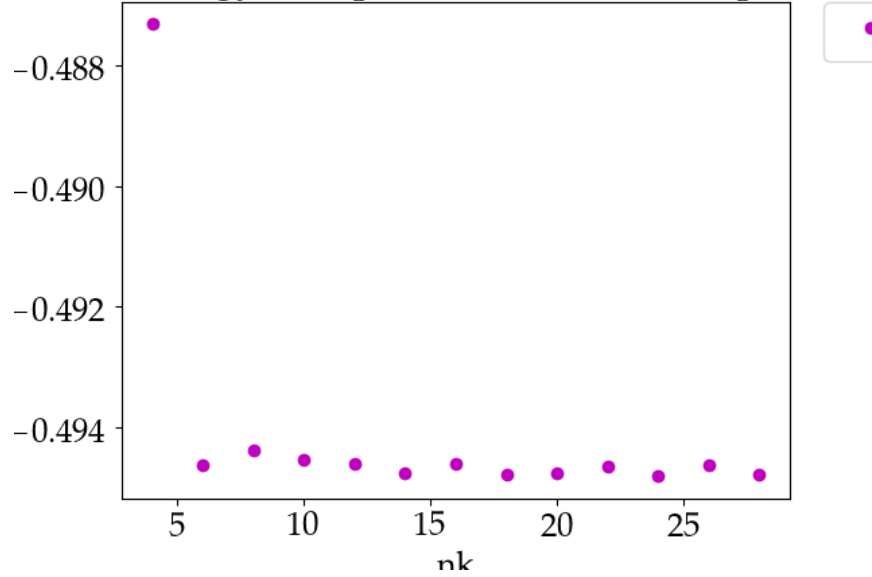


Figure 4: Variation of energy with k mesh.

- Conclusion: rmaxh only determines what atoms are its neighbours.
- This is the file which investigates this: `check_rmaxhenergynumberneighbours`
- Here is the data: Energy data for energy vs rmaxh rmaxh data for energy/ $n_{\text{neighbours}}$ vs rmaxh $n_{\text{neighbours}}$ for $n_{\text{neighbours}}$ vs rmaxh
- The output pictures are this:

1.8 DONE Show supercell of BOP working

1.9 DONE Check Stability Criteria

- Check if the matrix is complex
- Check if it is positive definite.

1.9.1 Results

- Without changing anything, the total energy of hcp in Tony's newest model is $E_{\text{tot hcp}} = -0.57230068\text{Ryd}$

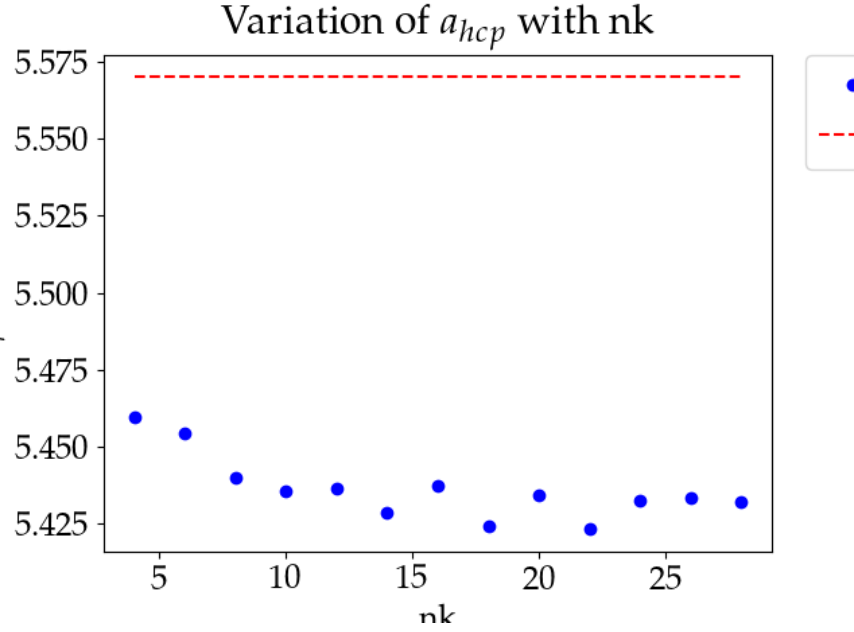


Figure 5: Variation of a_{hcp} with k mesh.

- I thought perhaps that the lattice parameters and the elastic constants that way might produce a different result.
- Minimising the lattice parameters gives an energy of $E_{tot\ hcp} = -0.572351\text{Ryd}$ with lattice parameters of $a_{hcp} = 5.4908\text{bohr}$, $c_{hcp} = 8.8353\text{bohr}$ giving $c/a_{hcp} = 1.6091\text{bohr}$
- Elastic constants, in GPa are

$$C_{11} = 185.4, C_{33} = 191.8, C_{44} = 39.7, C_{12} = 56.5, C_{13} = 56.1$$

- The stability criteria are still satisfied.

Checking Stability for the elastic constants.
 is C_ij matrix positive definite?: True

Criteria for stability:

$C_{11} - C_{12} > 0$
 True

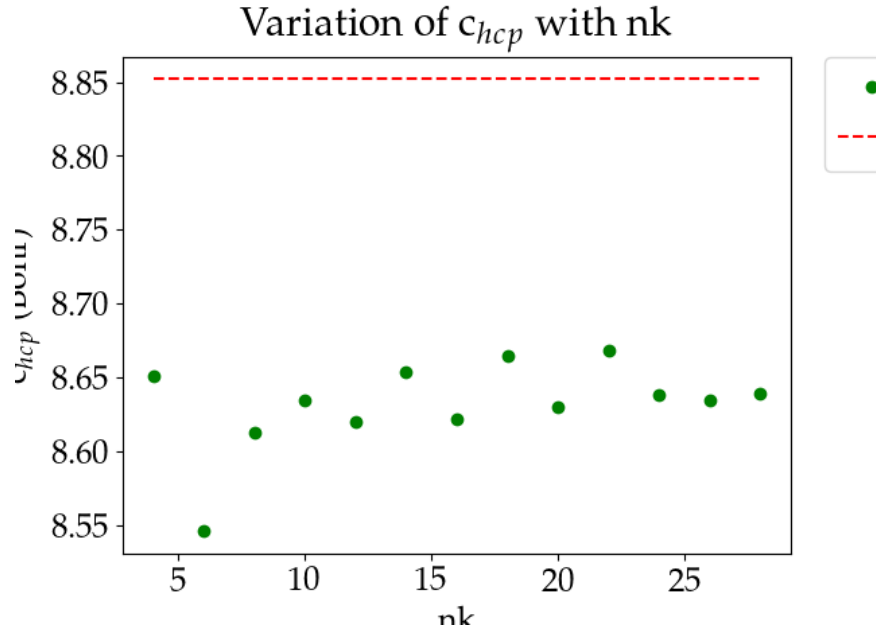


Figure 6: Variation of c_{hcp} with k mesh.

$$C_{11} + C_{12} + C_{33} > 0$$

True

$$(C_{11} + C_{12}) * C_{33} - 2 * C_{13}^2 > 0$$

True

$$C_{44} > 0$$

True

$$(C_{11} - C_{12}) > 0$$

True

$$(C_{11} + C_{12}) * C_{33} > 0$$

True

$$C_{11} + C_{12} > 0$$

True

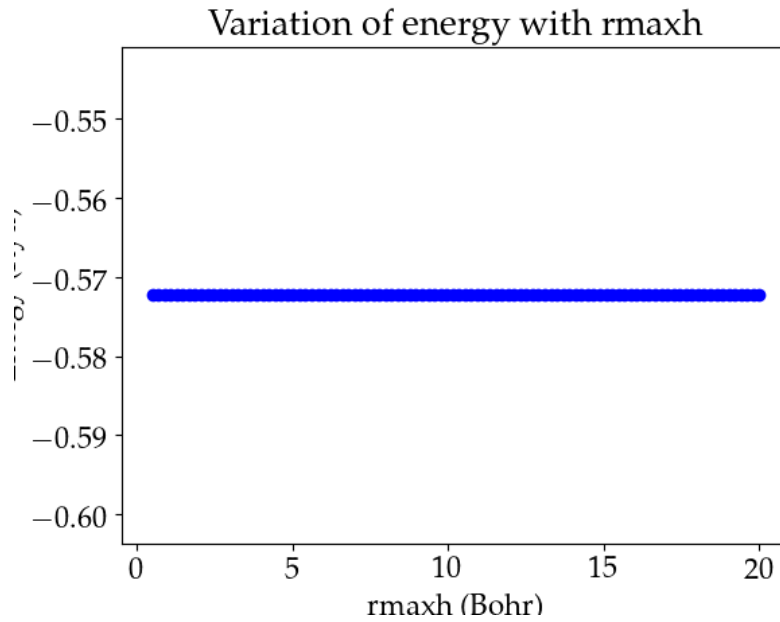


Figure 7: Variation of energy with change in rmaxh

```
C_33 > 0
True
```

```
C_11 > 0
True
```

1.10 DONE Build force constant matrix for hcp

- If the force constant matrix is positive definite then there shan't be any soft modes.

1.10.1 Results

- File used is `check_ecposdefinite.py`
- Using Fourth order $\mathcal{O}(h^4)$ formula for the mixed derivatives, one can

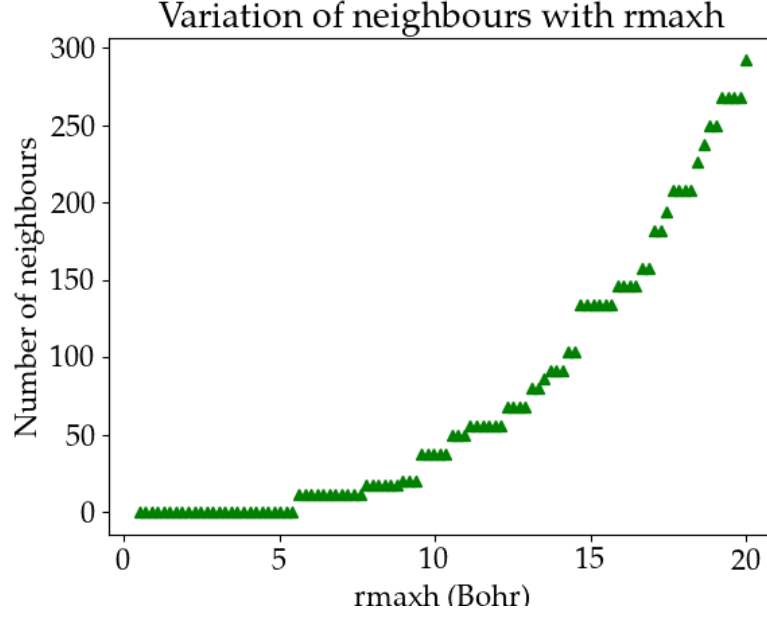


Figure 8: Variation of number of neighbours with change in rmaxh

find the 6×6 force constant matrix.

$$\frac{1}{144h^2}(8.(f_{1,-2} + f_{2,-1} + f_{-2,1} + f_{-1,2}) \quad (1)$$

$$- 8.(f_{-1,-2} + f_{-2,-1} + f_{1,2} + f_{2,1}) \quad (2)$$

$$- 1.(f_{2,-2} + f_{-2,2} - f_{-2,-2} - f_{2,2}) \quad (3)$$

$$+ 64.(f_{-1,-1} + f_{1,1} - f_{1,-1} - f_{-1,1})) \quad (4)$$

Eigenvalues

```
[-0.3173  0.3173  2.5963 -0.3185  0.3185 -2.5963]
```

Is force constant matrix positive definite? False

Force Constant Matrix

```
[[ 7.7099e-13  2.3901e-11 -2.3901e-11 -3.1729e-01  2.3901e-11 -2.3901e-11]
 [-7.7099e-13  0.0000e+00  0.0000e+00 -7.7099e-13 -3.1847e-01  0.0000e+00]
 [ 7.7099e-13  0.0000e+00  0.0000e+00  7.7099e-13  0.0000e+00  2.5963e+00]
 [-3.1729e-01 -2.5443e-11  2.5443e-11  2.5443e-11 -2.5443e-11  2.5443e-11]
 [-7.7099e-13 -3.1847e-01  0.0000e+00 -7.7099e-13  0.0000e+00  0.0000e+00]
 [ 7.7099e-13  0.0000e+00  2.5963e+00  7.7099e-13  0.0000e+00  0.0000e+00]]
```

- This matrix is not positive definite and so the structure is not stable.
- Using second order formula one obtains

Eigenvalues

```
[ 0.32 -0.32  2.545 -2.545  0.32 -0.32 ]
```

Is force constant matrix positive definite? False

Force Constant Matrix

```
[[ 0.    0.    0.   -0.32  0.    0.   ]
 [ 0.    0.    0.    0.   -0.32  0.   ]
 [ 0.    0.    0.    0.    0.   2.545]
 [-0.32  0.    0.    0.    0.    0.   ]
 [ 0.   -0.32  0.    0.    0.    0.   ]
 [ 0.    0.   2.545  0.    0.    0.   ]]
```

- Using another model we get another matrix that is not positive definite.

```
tbe ti -vhcp=1 -vfddtt=0.4668418806546737 -vqddstt=0.6660968695540497 -vb0tt=94.4
-vp0tt=1.1902574670213237 -vb1tt=-26.704816810939302 -vp1tt=0.9999600888309667
-vcr1=-6.158653986495596 -vcr2=3.9496749559495172 -vcr3=-1.0282840982939534
-vndt=1.992406298332605 -vahcp=5.5274 -vqq=1.5997394796830335 -vrmaxh=8.51 -vnk=3
```

Eigenvalues

```
[ 1.8512 -1.8512  0.2823 -0.2823 -0.281  0.281 ]
```

Is force constant matrix positive definite? False

Force Constant Matrix

```
[[ -2.4672e-13 -4.8572e-13 -5.0114e-13 -2.8232e-01  0.0000e+00  1.0618e-03]
 [ -4.8572e-13  0.0000e+00  0.0000e+00  0.0000e+00 -2.8103e-01  0.0000e+00]
 [ -5.0114e-13  0.0000e+00  0.0000e+00  1.0618e-03  0.0000e+00  1.8512e+00]
 [ -2.8232e-01  0.0000e+00  1.0618e-03 -2.5443e-13  0.0000e+00 -1.0618e-03]
 [  0.0000e+00 -2.8103e-01  2.4672e-13  0.0000e+00  0.0000e+00  0.0000e+00]
 [  1.0618e-03 -2.4672e-13  1.8512e+00 -1.0618e-03 -2.4672e-13 -7.4015e-13]]
```

- 1.11 **TODO** Make dislocations go through centre of triangle of atoms
- 1.12 **TODO** Investigate why the gamma surface minima are not along the lines joining the vectors.
- 1.13 **TODO** Change the lattice vectors to make the dislocation displacement fields periodic
- 1.14 **TODO** Make sure that the displacements are periodic
- 1.15 **TODO** Why is the displacement in the x direction in the graphs of create cells?
- 1.16 **TODO** Calculate the Internal elastic constants, like in Cousins

2 General notes

2.1 Dislocation arrays

Dislocation arrays are used within simulation cells to negate the effects of the long range strain fields produced from dislocations in the periodic array of cells one has in the simulation.

- Method of Clouet: Dislocation locking versus easy glide in titanium and zirconium. [?]
 - Introduced two dislocations into the simulation cell
 - This formed a quadrupolar periodic array of dislocations which minimises the elastic interaction between dislocations and their images.
 - This is because of the centrosymmetry of the Volterra elastic field, which means that the stress of this quadrupolar array ensures that the stress field created by the periodic image dislocations cancels locally at each dislocation position, thus limiting the perturbation of the dislocation core by the boundary conditions.
 - Arrangement is the same as the "S" arrangement found in [?]

2.1.1 Files to produce dislocations

1. Single Dislocations Here are the files used to produce single dislocations
Generate prismatic screw Ovito file prismatic screw from ovito

2. Quadrupolar arrangements

2.1.2 Bulatov and Cai: Computer simulations of dislocations

1. Sum of displacements from dipoles Simulating dislocation dipoles will introduce singularity in displacement between them. As we are not in the continuous case, this singularity is fine. However, the periodic boundary conditions are **not** satisfied, *i.e.* pair of dislocations forming a dipole will not be periodic along y , as the displacement field is not periodic along y .

This mismatch could relax away during energy minimization, but it is not guaranteed.

A naive way to try and remove this result is to try and construct a periodic displacement field from the non-periodic one generated, by the principle of linear superposition, but this does not work.

$$u_z^{\text{sum}} = \sum_{\mathbf{R}} u_z^{\text{inf}}(\mathbf{r} - \mathbf{R}) = u_z^{\text{inf}}(\mathbf{r}) + u_z^{\text{img}}(\mathbf{r})$$

$$u_z^{\text{img}}(\mathbf{r}) = \sum'_{\mathbf{R}} u_z^{\text{inf}}(\mathbf{r} - \mathbf{R})$$

where \mathbf{R} is a periodic vector of the two dimensional lattice vectors along x and y axes: $\mathbf{R} = n_1 \mathbf{c}_1 + n_2 \mathbf{c}_2$. $u_z^{\text{img}}(\mathbf{r})$ only accounts for **image** dipoles ($\mathbf{R} \neq 0$) whereas the other sum is the sum of all of them. This is because the sum of the displacements is *conditionally convergent*. This means that the ordering of the sum of the displacements will determine if the sum actually converges.

2. How to remove non-periodic displacements One can find the periodic displacement $u_z^{\text{textPBC}}(\mathbf{r})$ from the relation, which arises from the fact that $\partial_i \partial_j u_z^{\text{sum}}(\mathbf{r}) = \partial_i \partial_j u_z^{\text{PBC}}(\mathbf{r})$

$$u_z^{\text{textsum}}(\mathbf{r}) = u_z^{\text{textPBC}}(\mathbf{r}) + \mathbf{s} \cdot \mathbf{r} + \mathbf{u}_0$$

\mathbf{u}_0 is a constant term, so it can be ignored.

Recipe to remove the spurious non-periodic part of the displacement field:

- (a) Evaluate the conditionally convergent sum $u_z^{\text{sum}}(\mathbf{r})$, using an arbitrary truncation.

- (b) "Measure" the linear spurious part of the resulting field, using the equation below, by comparing it's values at four points in the periodic supercell from the above equation

$$u_z^{\text{err}}(\mathbf{r}) = \mathbf{s} \cdot \mathbf{r},$$

$$u_z^{\text{sum}}(\mathbf{r} + \mathbf{c}_i) - u_z^{\text{sum}}(\mathbf{r}) = \mathbf{s} \cdot \mathbf{c}_i,$$

where $i = 1, 2$.

- (c) Finally, subtract the linear term $u_z^{\text{err}}(\mathbf{r})$ from $u_z^{\text{sum}}(\mathbf{r})$ to obtain the corrected solution $u_z^{\text{PBC}}(\mathbf{r})$.

This procedure is independent of the truncation in the limit of large radius.

3. Adjusting the shape of the supercell When a dislocation dipole is introduced, there is a plastic strain that is generated.

$$\epsilon^{\text{pl}} = \frac{1}{2\Omega}(\mathbf{b} \otimes \mathbf{A} + \mathbf{A} \otimes \mathbf{b}),$$

where $\Omega = (\mathbf{c}_1 \times \mathbf{c}_2) \cdot \mathbf{c}_3$, and \mathbf{A} , is the vector normal to the plane of the plane connecting the dipoles and \mathbf{c}_i are the periodicity vectors.

In a supercell with fixed periodicity vectors, an increment in the plastic strain will be compensated by an oppositely signed increment of the elastic strain of the same magnitude: $\epsilon^{\text{el}} = -\epsilon^{\text{pl}}$.

In response to this elastic strain, there will be an internal *back-stress* acting to eliminate the source of the strain (i.e. the dislocation dipole). This back-stress may be large enough to push the dislocations back from their intended positions and may even lead to dislocation recombination.

Allowing for the simulation box to change shape during relaxation, one would see that it could reach a state of zero average internal stress. We can do this step **before relaxation**, such that we can accommodate/match the **plastic strain** produced by the dislocation dipole.

In the case study, the cut plane bounded by two dislocations is parallel to two of the repeat vectors, \mathbf{c}_1 and \mathbf{c}_3 . In this case the internal stress induced by the dipole can be removed by adjusting only the \mathbf{c}_2 repeat vector.

$$\mathbf{c}_2 \rightarrow \mathbf{c}_2 + \mathbf{b} \frac{A}{A_0},$$

If we say that $A_0 = |\mathbf{c}_3 \times \mathbf{c}_1|$ is the area of simulation box on the plane parallel to the dislocation dipoles, and A is the area that is between the dislocation dipoles in the simulation cell.

Adjusting this vector means that we have added an extra term $\mathbf{u}_z^{\text{tilt}}(\mathbf{r})$ to the solution of $\mathbf{u}_z^{\text{PBC}}(\mathbf{r})$ from before. In this study, it is

$$u_z^{\text{tilt}}(\mathbf{r}) = b \frac{Ay}{A_0 c_2},$$

where c_2 is the length of the periodicity vector before it has been tilted.

2.2 TBE Pair potentials and Bond integrals

2.2.1 Pair potentials in the code

- Pair potential is constructed by makvpp.f.
- This calls vppder.f which actually evaluates the pair potential at that point
- In makvpp.f, if in the range of $r_1 < r < r_c$, then augmentative/multiplicative polynomial is used.
 - To make this polynomial pcut45.f is used.
 - Depending on the degree of polynomial we have this structure:

```

rr = r1 - r2
xr1 = x - r1
xr2 = x - r2

c = val*rr*rr
if (n == 5) then
  pnorm = rr**(-5)
  a = (0.5d0*curv*rr - 3d0*slo)*rr + 6d0*val
  b = (slo*rr - 3d0*val)*rr
elseif (n == 4) then
  pnorm = rr**(-4)
  a = (0.5d0*curv*rr - 2d0*slo)*rr + 3d0*val
  b = (slo*rr - 2d0*val)*rr
p2 = pnorm*(c + xr1*(b + xr1*a))
dp2 = pnorm*(b + xr1*2d0*a)
ddp2 = pnorm*2d0*a
e = p2 * xr2**(n-2)

```



```

de = (xr2*dp2 + float(n-2)*p2) * xr2**(n-3)
dde = (xr2*xr2*ddp2+float(2*(n-2))*xr2*dp2+float((n-2)*(n-3))*p2)
C ... e, de and dde are the values and derivatives of the polynomial in the r

```

– So the form of the polynomial used is

*

$$P_5(x) = (x - r_2)^3 P_2(x)$$

*

$$P_2(x) = a(x - r_1)^2 + b(x - r_1) + c$$

*

$$a = \frac{1}{(r_1 - r_2)^5} \left\{ \frac{1}{2}(r_1 - r_2)^2 f''(r_1) - 3(r_1 - r_2) f'(r_1) + 6f(r_1) \right\}$$

*

$$b = \frac{1}{(r_1 - r_2)^4} \{ f'(r_1) * (r_1 - r_2) - 3f(r_1) \}$$

*

$$\frac{1}{(r_1 - r_2)^5} x$$

*

$$c = \frac{f(r_1)}{(r_1 - r_2)^3}$$

* Where $f(x)$ is the function that needs to be cut

- Current model has this

Ti,Ti:

```

type 2 (Exp. decay), V(d) = a exp (- b d)

```

	dds	ddp	ddd
coeff:	-2.75	1.84	-0.46
decay:	0.71	0.71	0.71

```

cutoff type 2 (multiplicative), 5th order polynomial, range [r1, rc]

```

	dds	ddp	ddd
r1:	6.20	6.20	6.20
rc:	8.50	8.50	8.50

2.2.2 Bond integrals from tbe

- So bond integrals from titanium look like this, from this file `plot_bondintegrals.py`

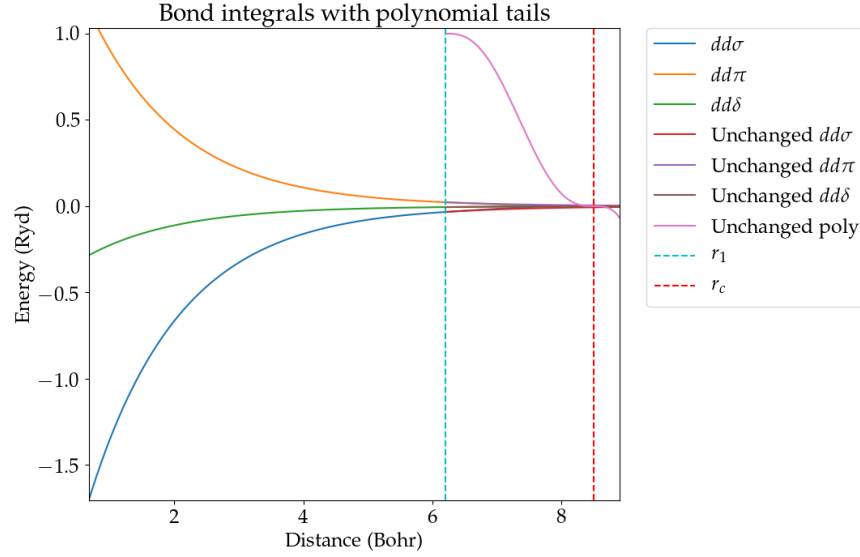


Figure 9: Bond integrals with multiplicative polynomial cutoffs.

2.2.3 Bond Integrals for first neighbour interaction

To make first neighbours it is optimal to have a cutoff that is within alat and $1.4 \times \text{alat}$. This is within the next shell of 6 neighbours and so having the cutoff between alat and $1.2 \times \text{alat}$ should be optimal.

2.3 Force constant matrix

2.3.1 Wallace

1. Crystal Potential: Introduction

- Since the vibrational energy of a crystal is generally considered to be small compared to its potential energy, the crystal potential is a first approximation to the free energy or the internal energy.
- Ions are labelled by the letters M and N .
- Equilibrium positions are given by the vectors $\mathbf{R}(M)$ and displacements from equilibrium are denoted by $\mathbf{U}(M)$.
- Potential energy of the crystal due to interactions among ions in

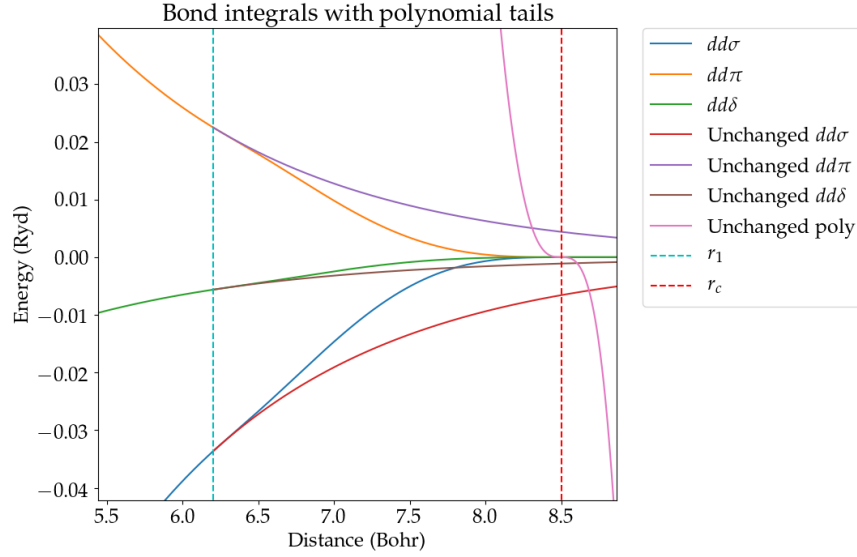


Figure 10: Bond integrals with multiplicative polynomial cutoffs: zoomed in.

a given configuration is given by Φ , which can be expanded as

$$\Phi = \Phi_0 + \sum_M \sum_i \Phi_i(M) U_i(M) \quad (5)$$

$$+ \frac{1}{2} \sum_{MN} \sum_{ij} \Phi_{ij}(M, N) U_i(M) U_j(N) \quad (6)$$

$$+ \frac{1}{3!} \sum_{MNP} \sum_{ijk} \Phi_{ijk}(M, N, P) U_i(M) U_j(N) U_k(P) \quad (7)$$

$$+ \frac{1}{4!} \sum_{MNPQ} \sum_{ijkl} \Phi_{ijkl}(M, N, P, Q) U_i(M) U_j(N) U_k(P) U_l(Q) + \dots \quad (8)$$

$$(9)$$

- $\Phi_i(M) = \frac{\partial \Phi}{\partial U_i(M)}$
- $\Phi_{ij}(M) = \frac{\partial^2 \Phi}{\partial U_i(M) \partial U_j(N)}$
- These are symmetric in their index pairs; *i.e.* $\Phi_{ij}(M, N) = \Phi_{ji}(N, M)$
- All of the coefficients are functions of the *initial* configuration.

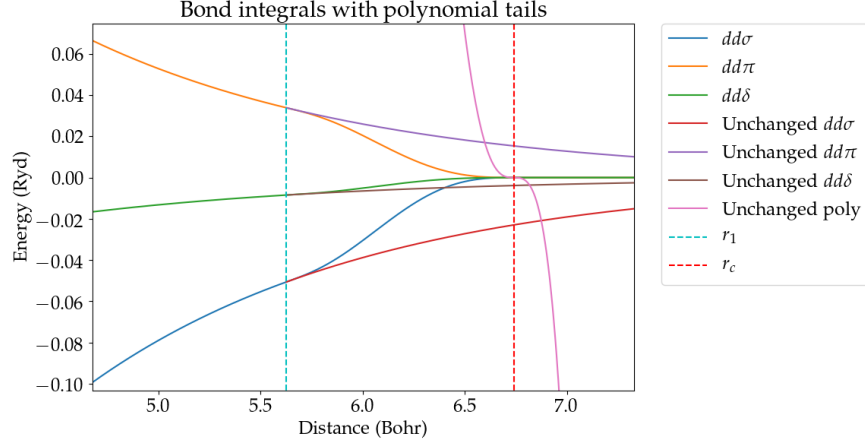


Figure 11: Bond integrals with multiplicative polynomial cutoffs for first neighbour interactions: zoomed in.

- This potential is supposed to represent the *entire* energy of the crystal except for the kinetic energy of the ions.
- From now on M, N represent the unit cell and μ, ν represent the individual ions in a given cell.
- The total potential of the system plus externally applied forces is Ψ . For a virtual process where the crystal is deformed while the externally applied forces are held constant Ψ is not conserved, if the forces are changed then it can be conserved.

$$\Psi = \Psi_0 + \sum_M \sum_i [\Phi_i(M) - f_i(M)] U_i(M) \quad (10)$$

$$+ \frac{1}{2} \sum_{MN} \sum_{ij} \Phi_{ij}(M, N) U_i(M) U_j(N) \dots \quad (11)$$

2. Stability and the Dynamical Matrix

- The equilibrium configuration of ions and external forces is a stable equilibrium if the total system potential is minimum with respect to small virtual displacements of the ions from equilibrium.

$$\Psi = \Psi_0 + \frac{1}{2} \sum_{MN} \sum_{ij} \Phi_{ij}(M, N) U_i(M) U_j(N) + \dots$$

- The stability condition is if they are positive definite: positive for any of the values $U_i(M)$, except if they are all 0.
- The stability condition is:

$$\sum_{\alpha\beta} \Phi_{\alpha\beta} U_{\alpha} U_{\beta} > 0$$

- $\alpha, \beta \dots$ are indices which refer to the pair Mi and > 0 means positive definite (all the eigenvalues are greater than zero).
- This is only satisfied if the matrix $\Phi_{\alpha\beta}$ is positive definite.

2.4 Gamma surfaces

2.4.1 Miscellaneous

- Seems like some atoms are missing in the site file when it is being read in to tbe.
- This means that there are some erroneous forces that make the program exit.
 - SOLUTION: Coordinates were not in units of alat.

2.4.2 Relaxing in tbe

- To relax in tbe need to modify:
 - Ewald tolerance: ewtol
 - * This can generally be set quite low: 1d-14
 - Convergence criteria:
 - * gtol: The tolerance in the force for convergence e.g. 1d-8
 - * xtol: The tolerance in the atomic position e.g. 1d-8.

2.4.3 Convergence and k-points in tbe

- Tony used a $30 \times 30 \times 30$ grid for the k-point mesh.
- Making a square cell, and increasing the length accordingly, one must reduce the number of k-points in that direction.
- Making a square cell with an increase of cell size along x to be $\sqrt{3}$, then we must reduce the k-point mesh by $n_{kx}/\sqrt{3} \approx 17.3 \approx 17$

- Therefore new grid is $17 \times 30 \times 30$

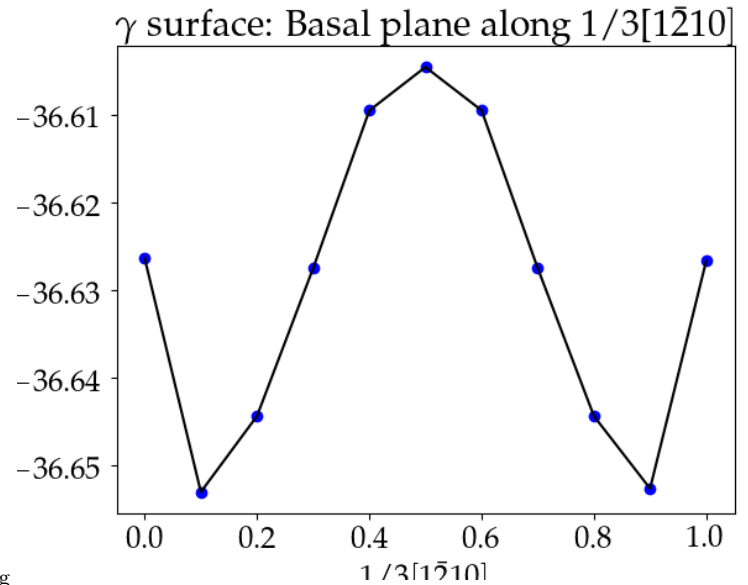
hcp cell type	Geometry	tetra	n atoms	nkx	nky	nkz	Maximum force	Total energy per at
Primitive	1x1x1	0	2	30	30	30	0.000000	-0.28614
Primitive	1x1x1	1	2	30	30	30	0.000001	-0.28614
Primitive	2x1x1	0	4	15	30	30	0.000001	-0.28614
Primitive	2x1x1	1	4	15	30	30	0.000511	-0.28614
Primitive	4x2x8	0	128	8	15	4	0.000061	-0.28615
Primitive	4x2x8	1	128	8	15	4	0.000118	-0.28615
Primitive	4x2x8	0	128	9	15	4	0.000063	-0.28614
Basal Square	1x1x1	0	4	16	30	30	0.000065	-0.28614
Basal Square	1x1x1	0	4	17	30	30	0.000064	-0.28615
Basal Square	1x1x1	0	4	18	30	30	0.000043	-0.28614
Basal Square	1x1x1	0	4	19	30	30	0.000054	-0.28615
Basal Square	1x2x8	0	64	15	15	30	0.000083	-0.28615
Basal Square	1x2x8	0	64	16	15	30	0.000020	-0.28614
Basal Square	1x2x8	0	64	17	15	30	0.000061	-0.28615
Basal Square	1x2x8	0	64	18	15	30	0.000057	-0.28614
Basal Square	1x2x8	0	64	15	15	4	0.000065	-0.28615
Basal Square	1x2x8	0	64	16	15	4	0.000028	-0.28614
Basal Square	1x2x8	0	64	17	15	4	0.000044	-0.28615
Basal Square	1x2x8	0	64	18	15	4	0.000052	-0.28614
Basal Square	1x2x10	0	80	15	15	3	0.000087	-0.28615
Basal Square	1x2x10	0	80	16	15	3	0.000065	-0.28614
Basal Square	1x2x10	0	80	17	15	3	0.000064	-0.28615
Basal Square	1x2x10	0	80	18	15	3	0.000052	-0.28614

Less precise c/a below.

Basal Square	1x1x1	0	4	18	30	30	0.000043	-0.28614662	-0.93605957	0.18636601
Basal Square	1x1x1	1	4	18	30	30	0.000097	-0.28614928	-0.93606369	0.18636601
Basal Square	1x1x1	0	4	17	30	30	0.000064	-0.28615864	-0.93607342	0.18636601
Basal Square	1x1x1	1	4	17	30	30	0.000024	-0.28615254	-0.93606731	0.18636601
Basal Square:	2x2x8	0	128	9	15	4	0.000052	-0.28614359	-0.93605835	0.18366000
Basal Square:	2x2x8	1	128	9	15	4	0.000121	-0.28614669	-0.93606145	0.18636600
Basal Square:	1x1x8	0	32	17	30	4	0.000044	-0.28615651	-0.93607127	0.18636600
Basal Square:	1x1x9	0	36	17	30	4	0.000058	-0.28615716	-0.93607192	0.18636600
Basal Square:	1x1x9	0	36	17	30	3	0.000071	-0.28615681	-0.93607157	0.18636600

2.4.4 Results

- Have now done the gamma line along $1/3[1\bar{2}10]$, but the end points do not seem quite right.



- File and data: basal_{energyplotting}
- Basal plot $8 \times 8 \times 8$
- Basal Plane gamma surface
- plot_{hbgs}, energy, x, y

2.4.5 Literature Review

1. General notes on dislocations
 - Dislocations have areas of tension (distance between atoms is larger than the lattice vector) and compression (distance is less than the lattice vector)
 - A reasonable value for the dislocation core radius r_0 therefore lies in the range \mathbf{b} to $4\mathbf{b}$, i.e. $r_0 \geq 1nm$ in most cases.
2. How do stacking faults occur? Stacking faults can occur:
 - During crystal growth
 - As part of other defects (e.g. dislocations)

- As evolution of other defects.
 - There can be vacancy agglomeration, such that there is a vacancy disk, creating a stacking fault if the disk is large enough for the two surfaces to collapse together.
 - Example of this is that these vacancy disks condense and are then bordered by an edge dislocation.

3. Types of stacking faults.

- Disk of vacancies: *intrinsic* stacking fault.
- Interstitial agglomeration: *extrinsic* stacking fault.
- Both are bordered by an edge dislocation.
 - These are *partial* dislocations.
 - In fcc these are Frank partials of burgers vector $\mathbf{b} = \pm \frac{a}{3} \langle 111 \rangle$

(a) Types of stacking faults in hcp

- Intrinsic 1 (I_1) = (ABAB|CBCB) – Basal plane
- Intrinsic 2 (I_2) = (ABAB|CACA) – Basal plane
- Extrinsic (I_E) = (ABAB|C|ABAB) – Basal plane
- Easy prismatic $F_1 = \mathbf{b}/2$
 - This energy corresponds to a true metastable stacking fault but has only been seen in the case of DFT so far.

4. Partial dislocations

- Partial dislocations *must* be bordered by a two dimensional defect: usually a stacking fault.
 - (Think of double ended pencil slice, where dislocation lines are the border of the pencil and the plane is the stacking fault.)
- Shockley dislocations:
 - Cut and weld but don't fill in (to finish full Volterra procedure.)
 - Produce intrinsic stacking fault.
 - These can glide on the same plane as the perfect dislocation, and can also change length.

- Frank partials bound loop and so can only move on their glide cylinder. Changing length would involve absorption or emission of point defects.

5. Energy considerations with stacking faults and partials.

- Have energy gain from splitting into two smaller burgers vectors
- Interaction energy of two partials will be large at smaller distances
- but also, stacking fault energy is per unit length, so this would minimise the distance
- So have an equilibrium distance between the partials.
- This makes dislocations like ribbons that stretch through the material.
- These ribbons can undergo constrictions from jogs
- Reason that stacking faults are not observed in bcc structures are just that the stacking fault energies are too high. (Because of dense packing?)

6. Gamma surfaces in DFT

- (a) [Benoit, Tarrat and Morillo 2012] Density functional theory investigations of titanium γ -surfaces and stacking faults.
- Comparison between central force embedded atom interactions, N-body central force, N-body angular, empirical potentials, tight binding and DFT pseudopotential and DFT full electron calculations.
 - Cauchy pressures are deemed to be N-body effects but really for Cauchy pressures that are accurate one needs a volume-dependent energy term which makes elastic constant contributions. **Needs more investigation**
 - Legrand suggests that there is an energetic favouring of the prismatic plane for these stacking fault energies due to the directional covalent d-orbital bonding in transition metals.
 - He also suggested a ratio to measure this

$$R = \frac{\gamma_b/C_{44}}{\gamma_p/C_{66}}$$

- Suggests that large fitting database of configurations far from the ideal hcp lattice might provide accurate reproduction of dislocation core structure.
- Not systematic improvement going from N-body central force potentials to TB.
- Inversion in strength between C_{66} and C_{44} in the BOP calculations of Girshick and Pettifor
 - So it was stipulated that the N-body effects of this model were not well accounted for.
- Free surfaces were introduced into the slab geometry to avoid problems of asymmetric configuration of stacking faults in periodic images.
- Oscillations in the stacking fault energy with the number of slabs are due to quantum size effects.
- Underestimation of the energy of basal faults and overestimation of the prismatic easy excess energy lead to an inversion between the basal and prismatic easy faults in terms of energetic preference. This was also seen in the BOP model.
 - Not sure how this works. The Cauchy pressure was fitted to in certain BOP models. Maybe this was only used in Stefan Znam's case and not any others. It would be interesting to see if his model stands up against this criteria.
- No models other than DFT produced a metastable stacking fault energy at the prismatic easy fault.

2.5 Notes on Thermodynamics and Stability

2.5.1 Wallace 1972

- For hexagonal materials, there are general stability requirements:
 - $C_{11} - C_{12} > 0$
 - $C_{11} + C_{12} + C_{33} > 0$
 - $(C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0$
 - $C_{44} > 0$
 - $C_{66} = \frac{1}{2}(C_{11} - C_{12}) > 0$
 - $(C_{11} + C_{12})C_{33} > 0$
 - $C_{11} + C_{12} > 0$

- $C_{33} > 0$
- $C_{11} > 0$
- The equilibrium configuration of ions plus external forces is a stable equilibrium if the total system potential Ψ is minimum with respect to small virtual displacements of ions from equilibrium.
- Cauchy relations (at least in the cubic case) will be destroyed if non-central forces are included in the crystal potential.

2.5.2 Fast, Will, Johansson: Elastic constants in hexagonal transition metals

1. Cauchy Relations

- Cauchy relations for hexagonal materials:
 - $C_{13} = C_{44}$
 - $C_{12} = C_{66} = \frac{1}{2}(C_{11} - C_{12})$
- These only are meant to hold for central forces.
- These Cauchy forces have been shown to hold more in hexagonal materials rather than cubic ones.
- In cubic materials sometimes one finds C_{44} four times smaller than C_{12} .
- They showed the Cauchy ratios:
 - C_{12}/C_{66}
 - C_{13}/C_{44}
- The Cauchy relations were close to 1 apart from calculations with Co, Zr and Ti, where it was closer to 2.
- These are smaller than the 3/4 times deviations in cubic crystals.

2. Normalised elastic constant

- To investigate Cauchy relations fully they used a normalised elastic constant which was obtained by dividing by the bulk modulus: $C'_{ij} = C_{ij}/B$
- It becomes easier to study trends as one is normalising the interatomic forces with an average restoring force of the system, when dividing by the bulk modulus.
- Suggest that the hexagonal materials are quite isotropic.

2.6 Notes on Tight Binding and BOP Models

2.6.1 Pair correlation and cutoffs

- Analysing the pair correlation function in ovito, it seems reasonable that one should have cutoffs, if $a = 2.95$ and $c = 4.683$ to give a $c/a = 1.587$, of 4.7, as this is past the third neighbour distance.
- This was done in Znam's thesis.
- At the moment we are cutting off at 8.5ryd , which gives the neighbours to be 20, so we are actually not including a multiple of the coordination for the neighbour table, which may give a weird structure by symmetry.
- Another reason is that in the model for Titania, the Ti-Ti integrals were given a longer cutoff to stabilise the rutile and anatase structures.
- The TB Iron model has a cutoff which is twice the lattice parameter.

2.6.2 Trinkle 2006

- Collapse problem found in tight binding if atoms come too close together. Electrons go in the bonding state and not the anti-bonding state and so the energy goes down
- Can be fixed by implementing spline potential that levels off below a given cutoff, which effectively simulates a pair potential.
- Environmentally dependent on-site terms were used instead of a pair potential.
- These on-site energies are dependent on the local density ρ_i and they have a cutoff function $f_c(r_{ij})$ which has fixed parameters R_0 and l_0 .

$$\epsilon_{i,l} = a_l + b_l \rho_i^{2/3} + c_l \rho_i^{4/3} + d_l \rho_i^2$$

$$\rho_i = \sum_{j \neq i} \exp\{-\lambda^2 r_{ij} f_c(r_{ij})\}$$

$$f_c(r) = \frac{1}{1 + \exp\left\{\frac{r-R_0}{l_0}\right\}}$$

2.6.3 Stefan Znam 2001 Thesis

1. Cauchy Pressures

- Cauchy pressures have zero contribution from pair potentials at equilibrium.
- Generally all Cauchy pressures in many-body central force models, describing atoms embedded in an electron gas of the surrounding neighbours, are positive when experimentally they are negative.
 - This is the case with EAM and Finnis-Sinclair models.
- In TiAl the environmental screening effects are most profound in the case of s and p orbital overlap repulsion, as these orbitals are being squeezed into the core region under the influence of unsaturated covalent d bonds.

(a) Reason for Cauchy Pressures

- The reason for negative Cauchy pressures is meant to be from covalent character of d bonding, but when using tight binding models, which account for this, the Cauchy pressure issue is not resolved.
- These effects are explained in detail with regards to tight binding in Nguyen-Manh, Pettifor, Znam, Vitek: Negative Cauchy Pressure Within The Tight-Binding Approximation.
- This warrants the need for environmental terms:
 - The physical reasoning behind these terms are due to the repulsion between orbitals in the atom.

(b) Why TB can't have negative Cauchy Pressures

- TB only has contributions from the bond part of the interactions as the pair potential at equilibrium has no contribution to the Cauchy Pressures.
- Failure of TB to reproduce negative Cauchy pressures because the orbitals are tightly bound: interactions extend out only to nearest neighbour atoms.
- This requires that orbitals are not *unscreened* atomic orbitals.
- Orbitals must be screened.
- For transition metals, the valence d orbitals aren't screened as they are tightly bound anyway.

(c) Thoughts: What does this mean for Tight Binding

- As the Cauchy pressure contributions only come from the bond integrals and the pair potential, then the reason that some of the Cauchy pressures are off are because these terms might not be necessarily correct.
- There are screening of these bond integrals, hence the Yukawa terms, which change the interaction of these bond integrals.
- These classical environmental terms modify the elastic constants by including physically motivated screening terms in terms in terms of Ti-Al as there is some repulsion from s-p overlap, as these orbitals are squeezed into the core from the unsaturated d bonds.
- These *reduce* the Cauchy pressures such that they are negative ()

2.7 Ti Swarm fitting.

- Here used fitting with uniform weights across all target quantities without a regularisation of the parameters.
- It can be seen that the lattice parameters aren't as good as they could be. This calls for the use of weighted parameters.
- Have now started weighted parameter search for the best parameters with regards to titanium.

Build Objective Function

...with L1 norm

Objective **function**: 563

Objective **Function** = 563.2340263379571

Stopping search: Swarm best position change less than 1e-08

[0.34606728 -0.22330935 65.79555644 0.52284417 0. -0.62229341 1.98315066]

563.2340263379571

Quantity	predicted	target	squared diff.	p _{norm}	weight	objective
a _{hcp} :	4.744693	5.576790	0.692385	0.832097	1.000000	1.524483
c _{hcp} :	7.495518	8.852101	1.840316	1.356583	1.000000	3.196899
c ₁₁ :	174.924630	176.100000	1.381495	1.175370	1.000000	2.556865
c ₃₃ :	190.161490	190.500000	0.114589	0.338510	1.000000	0.453099
c ₄₄ :	54.517320	50.800000	13.818465	3.717320	1.000000	17.535784
c ₁₂ :	65.010403	86.900000	479.154446	21.889597	1.000000	501.044043
c ₁₃ :	73.335501	68.300000	25.356271	5.035501	1.000000	30.391772
a _{omega} :	7.331279	8.732543	1.963543	1.401265	1.000000	3.364808
c _{omega} :	4.768459	5.323431	0.307994	0.554972	1.000000	0.862966
u _{omega} :	1.000025	1.000000	0.000000	0.000025	1.000000	0.000025
DeltaE _{O_{hcp}} :	-1.170318	-0.734754	0.189716	0.435564	1.000000	0.625281
a _{bcc} :	5.331467	6.179489	0.719140	0.848021	1.000000	1.567162
bandwidth:	0.325300	0.426000	0.010140	0.100700	1.000000	0.

2.7.1 Fitting varying the canonical weights.

rmaxh was set to 8.51, as this is the maximum range of the cutoff.

Quantity	predicted	target	squared diff.	p _{norm}	weight	objective
a _{hcp}	5.533022	5.576790	0.001916	0.043768	1000.000000	45.683665
c _{hcp}	8.850424	8.852101	0.000003	0.001677	1000.000000	1.680027
c ₁₁	182.244765	176.100000	37.758133	6.144765	1.000000	43.902897
c ₃₃	188.810134	190.500000	2.855646	1.689866	1.000000	4.545512
c ₄₄	39.062885	50.800000	137.759875	11.737115	1.000000	149.496991
c ₁₂	68.120096	86.900000	352.684798	18.779904	1.000000	371.464703
c ₁₃	68.010464	68.300000	0.083831	0.289536	1.000000	0.373367
a _{omega}	8.670219	8.732543	0.003884	0.062324	250.000000	16.552204
c _{omega}	5.402550	5.323431	0.006260	0.079119	250.000000	21.344836
u _{omega}	0.999970	1.000000	0.000000	0.000030	1.000000	0.000030
DE (o, hcp)	-2.451465	-0.734754	2.947097	1.716711	1.000000	4.663808
a _{bcc}	6.293291	6.179489	0.012951	0.113803	500.000000	63.376810
bandwidth	0.493300	0.426000	0.004529	0.067300	1000.000000	71.829290

fddtt=0.46858665192192056 qddstt=0.6675934593368511

b0tt=94.48656458962752 p0tt=1.1904330020322709 b1tt=-26.68382995150727 p1tt=0.99996079

cr1=-6.159908080507984 cr2=3.949841729455178 cr3=-1.0282365318567852 ndt=1.992439034070

Objective function: 794

```

Objective Function = 794.9141378839079
Stopping search: Swarm best position change less than 1e-08
[ 4.68586652e-01 -4.04075885e-01  9.44865646e+01  1.74317108e-01
 -2.66838300e+01 -3.92062406e-05  1.99243903e+00 -6.15990808e+00
  3.94984173e+00 -1.02823653e+00]
794.9141378839079

```

2.8 DFT

Run:

- `lmchk -getwsr ti`
- Copy the old `rmax` into the `R` category in `SPEC`
- `lmfa ti -vhcp=1`
- Copy `baspo` to `basp`
- Run `lmf`

2.9 Python

2.9.1 OS

Use `OS` module rather than making a load of files to a certain directory.

```

import os
##### Current working directory #####
# detect the current working directory and print it
path = os.getcwd()
print ("The current working directory is %s" % path)

##### Directories #####
# define the name of the directory to be created
path = "/tmp/year"

try:
    os.mkdir(path)
except OSError:
    print ("Creation of the directory %s failed" % path)
else:
    print ("Successfully created the directory %s " % path)

```



```
##### Subdirectories #####
# define the name of the directory to be created
path = "/tmp/year/month/week/day"

try:
    os.makedirs(path)
except OSError:
    print ("Creation of the directory %s failed" % path)
else:
    print ("Successfully created the directory %s" % path)
```

2.9.2 Shelve

Use the shelve module to store multiple objects.

To write in:

```
import shelve

integers = [1, 2, 3, 4, 5]

# If you're using Python 2.7, import contextlib and use
# the line:
# with contextlib.closing(shelve.open('shelf-example', 'c')) as shelf:
with shelve.open('shelf-example', 'c') as shelf:
    shelf['ints'] = integers
```

To extract values:

```
import shelve

# If you're using Python 2.7, import contextlib and use
# the line:
# with contextlib.closing(shelve.open('shelf-example', 'r')) as shelf:
with shelve.open('shelf-example', 'r') as shelf:
    for key in shelf.keys():
        print(repr(key), repr(shelf[key]))
```

3 DFT Lectures UCL

3.1 David Bowler O(N) DFT

3.1.1 Types of Exchange-correlation Functionals

1. LDA

- The electron density is the same as a uniform electron gas.
- Exchange is Slater.
- Still parameterised (Ceperly). Parameters from Quantum Monte-Carlo calculations.

2. GGA

- The gradient of the electron density is included in functional.
- Have the reduced density

$$\frac{\nabla n(\mathbf{r})}{n(\mathbf{r})}$$

(a) Perdew-Burke-Ernzerhof

•

$$E_x = \int n(\mathbf{r}) \epsilon_{xc}[n(\mathbf{r})] F_x(S) d\mathbf{r}$$

•

$$E_c = \int n[\epsilon_c + H(n, S)] d\mathbf{r}$$

- These integrals are then fitted to various limits.

3. Hybrid Functionals

- These are functionals to correct the self-interaction energy that is apparent in the previously mentioned functionals.
- The Hartree term

$$V_H = \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}$$

- The exchange term cancels the self interaction.
- Generally only a part of this Hartree-Fock calculation is included in the function otherwise it is not stable.

DFT speed is limited by how it can find the energies of the system we are interested in. Diagonalisation is inherently an $\mathcal{O}(N^3)$ process.

To actually build the hamiltonian it is of $\mathcal{O}(N^2)$. Solving is $\mathcal{O}(N^3)$.

How do we solve for DFT? Generally it depends on the choice of functional we have. Hybrid functionals almost scale as $\mathcal{O}(N^4)$ due to the inclusion of exact exchange interaction by Hartree-Fock. Because of this exact exchange, there are better band gaps .

The $\mathcal{O}(N)$ DFT generally comes because of the manipulation of sparse matrices. Insead of matrix multiplication being of $\mathcal{O}(N^3)$ we can have matrix multiplication being of $\mathcal{O}(N)$.

The reason we can essentially do $\mathcal{O}(N)$ is that in the Kohn-Sham equations, the density is actually a local function ($n(\mathbf{r})$, not $n(\mathbf{r} - \mathbf{r}')$) This means that in theory we can actually have a theory which sufficiently describes the dynamics of a given system with an electron density that is local in space. In many DFT codes however, the electron density is non-local ($n(\mathbf{r} - \mathbf{r}')$), and this slows down the calculation. To actually make it $\mathcal{O}(N)$, we have to have range cutoffs for the interactions of the atoms. This means that the hamiltonian is sparse as quite a lot of the elements are zero such that we can use methods that involve $\mathcal{O}(N)$ multiplication.

When it comes to Structural relaxation there are a few things that come to mind when structures are not converging: there is usually only one atom that has some huge force on it. Consider the boundary conditions.

For faster diagonalisation of the hamiltonian matrix it may be useful to look at methods such as Krylov-Subsapace, Lanczos and folded-spectrum methods.

3.2 Jochen Blumberger: Molecular dynamics

3.2.1 Introduction

- Molecular dynamics is important. (Even at 0K there is a zero point energy of vibration).
- Need theory to see how atoms move

3.2.2 Born-Oppenheimer approximation

- Have hamiltonian that consists of interaction between:

- nucleus-nucleus
- nucleus-electron
- electron-electron
- First assumption is that we can write the eigenfunction of this large hamiltonian as a product state consisting of an electronic ground state and nuclear eigenstate.
- Second approximation is that we are able to say, as the mass of the ion $M_I \sim 1000m_e$ then we can say that the kinetic energy term of with regard to the nucleus positions will be small.
- From this we can say that the action of this nuclear kinetic energy operator on the electronic eigenstate is small.
- This means we can neglect the **electronic** wavefunction, and work with the equation

$$\hat{H}\Phi(\mathbf{R}) = E_{\mathbf{R}}^0\Phi(\mathbf{R})$$

- Where $E_{\mathbf{R}}^0$ is the ground state energy hypersurface from the electronic wavefunction. We get this from DFT calculations.
- Even now we can only really calculate 8 degrees of freedom for the Nuclear wavefunction.

3.2.3 Molecular Dynamics

1. Verlet Algorithm

- This algorithm simply uses the forward and backward derivative of the nuclear positions and adds them together to get a formula for the positon.

$$\mathbf{R}_I(t + \delta t) = 2\mathbf{R}_I - \mathbf{R}_I(t - \delta t) + \frac{f_I(t)}{M_I}\delta t^2 + \mathcal{O}(\delta t^4)$$

$$\dot{\mathbf{R}}_I(t) = \frac{1}{2\delta t}[\mathbf{R}_I(t + \delta t) - \mathbf{R}_I(t - \delta t)] + \mathcal{O}(\delta t^3)$$

- This causes a problem however: the velocity is calculated a step after that of the positons. So this leads to the Velocity Verlet algorithm.

- The timestep for these algorithms is on the order of $1fs$, such that one can have adequate resolution of atomic vibrations ($fs \sim 10^{-14}s^{-1}$, so period is around $10fs$)

2. Velocity Verlet Algorithm

- For this algorithm the forward derivative with respect to nuclear positions is used with a calculation of the force at a later time.
- Then the Taylor expansion of the position at time t is used with the terms of later time.

•

$$\mathbf{R}_I(t + \delta t) = \mathbf{R}_I(t) + \dot{\mathbf{R}}_I \delta t + \frac{f_I(t)}{M_I} \delta t^2 + \mathcal{O}(\delta t^3)$$

•

$$\dot{\mathbf{R}}_I(t + \delta t) = \dot{\mathbf{R}}_I(t) + \frac{1}{2M_I} [f_I(t + \delta t) + f_I(t)] \delta t + \mathcal{O}(\delta t^3)$$

3. How to calculate the forces

- Use the Hellmann-Feynman theorem.

–

$$\mathbf{f}_I = \langle \psi_{\mathbf{R}}^0 | \frac{\partial}{\partial \mathbf{R}_I} \hat{H} | \psi_{\mathbf{R}}^0 \rangle$$

- This is derived using the parameter λ , assuming that the Hamiltonian depends on this λ .

4. Carr-Parinello MD

- This is a form of molecular dynamics where both the positions and the orbitals are used as dynamical variables.
- An *orbital velocity* and (orbital mass) is defined.
- Using this one can create trajectories that propagate both the ionic positions and orbitals in time.
- This circumvents the need for self-consistent cycles to obtain the correct orbitals, but:
 - The dynamics are not always in the ground state energy.
 - The necessary time step is decreased by about 3 – 4 times (speed increase is 5–10 times from removal of self-consistency)

3.3 Matteo Salvalgio: Enhanced Sampling

3.3.1 Introduction

- Have a phase space that is $6N$ dimensional (3 spatial positions and 3 components of momenta).
- Each point in this phase space is a microstate.
- The microstates sampled are from the Canonical Ensemble (N, V, T) .
- Can define partition function

$$Q(N, V, T) = \frac{1}{N!h^{3N}} \int dx e^{-\beta \mathbf{H}(\mathbf{x})}$$

- Can have thermodynamic potential defined from this:

$$A(N, V, T) = -k_B \ln(Q(N, V, T))$$

- What we really want to do is obtain an observable quantity from this high dimensional space.

3.3.2 Ergodic principle

- This is the principle which states that the amount of time that microstates of the same energy spend in a configuration is proportional to the volume of phase space they occupy.
- In other words, every microstate is equiprobable.
- So the observable quantity:

$$O = \langle O \rangle = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt O(x(t)),$$

where $O(x(t))$ is the instantaneous realisation of $O(x)$

3.3.3 Collective variables

- Collective variables are just functions that depend on the coordinates (CVs) $S(\mathbf{R})$
- Given a collective variable we can define a probability density $p(S)$

- So

$$p(S) = \int d\mathbf{R} [\delta(S(\mathbf{R}) - S)] p(\mathbf{R})$$

-

$$p(\mathbf{R}) = \frac{e^{-\beta U(\mathbf{R})}}{\int e^{-\beta U(\mathbf{R})} d\mathbf{R}},$$

where the denominator is the configuration integral \mathcal{Z}

1. Calculating free energies from collective variables

- Free energy profile is then just

$$F(S) = -k_B T \ln(p(S))$$

- The free energy change between configurations A and B are then just

$$\Delta F_{AB} = -k_B T \ln \left\{ \frac{\int_B p(S) dS}{\int_A p(S) dS} \right\}$$

- Can think of these configurations as spikes in $p(S)$ and troughs in $F(S)$, with some form of energy barrier between them. This region can then be split in to regions belonging to A and B, from which the separate integrations can be evaluated.
- This energy barrier is on the order of kT
- If not, then simulation times will be very large to be able to obtain a result that obeys ergodicity.
- Can use a biased potential for the sampling and work backwards to obtain the actual probability density.

3.3.4 Biased Potentials

- Biased potentials can be used to reconstruct the Free energy landscape of a system with respect to its collective variables.
- It does this by using a potential that reduces or removes the free energy barrier such that different parts of the phase space can be explored.
- From this, the whole of the phase space in consideration can be explored such that the probability distribution with respect to a collective variable $p^b(S(R))$ can be found.

- This probability distribution is related to the unbiased probability distribution $p^U(S(R))$.
1. Introduction to Biased Potentials Two main equations: The configuration integral \mathcal{Z} and the {Absolute Free Energy} $\mathcal{A}(N, V, T)$:

$$\mathcal{Z} = \int e^{-\beta U(R)} dR$$

$$\mathcal{A}(N, V, T) = -\frac{1}{\beta} \ln\{\mathcal{Z}\}$$

Considering two different systems A and B , with two different potential energy functions $U_A(R)$ and $U_B(R)$, we can have separate configurational integrals \mathcal{Z}_A and \mathcal{Z}_B as per the definition above.

Then, we can actually perturbate with respect to another variable defining $\Delta U_{BA}(R) = U_B(R) - U_A(R)$

$$\mathcal{Z}_B = \frac{\mathcal{Z}_B \mathcal{Z}_A}{\mathcal{Z}_A} = \mathcal{Z}_A \langle e^{-\beta \Delta U_{BA}(R)} \rangle_A$$

The last term is the ensemble average with respect to A This means we can express the free energy difference (Zwanzig 1953)

$$\Delta \mathcal{A}_{AB} = -k_B T \ln \left(\frac{\mathcal{Z}_B}{\mathcal{Z}_A} \right) \quad (12)$$

$$= -k_B T \ln \langle e^{-\beta \Delta U_{BA}(R)} \rangle_A \quad (13)$$

To sample this efficiently we can use biased potentials.

$$U_{\text{tot}} = U_0(R) + V(S(R)),$$

where $V(S(R))$ is the biased potential which is a function of the collective variables.

We can define a partition function:

$$Q_{\text{tot}} = Q_0 \langle e^{-\beta V(S(R))} \rangle_0$$

Can express the actual probability density of the system in terms of a biased potential

$$p^u(S(R)) = p^b(S(R)) e^{\beta V(S(R))} \langle e^{-\beta V} \rangle_0$$

where u and b denote unbiased and biased configurations.

This gives the free energy as

$$F(S(R)) = -k_B T \ln\{p^b(S(R))\} - V(S(R)) \quad (14)$$

$$- k_B T \ln\{\langle e^{-\beta V} \rangle_0\}, \quad (15)$$

where the term on the second line is a constant.

2. Umbrella sampling If we don't know the shape of the free energy surface then we can use *Umbrella Sampling*. If we know for example, two metastable states that we want to sample then we can make a pathway between them using this method.

Umbrella sampling defines a series of biases simulations (*windows*) such that one can reconstruct the free energy surface. These simulations must have probability distributions that overlap.

When one goes through the process of umbrella sampling, naively going through the reconstruction of the free energy surface gives a poor reconstruction. It is necessary that weights are in place such that the reconstruction of the global free energy profile is smooth.

$$F(S(R)) = -k_B T \ln\{p^b(S(R))\} - V(S(R)) + C_i,$$

$$p_i = p_i^b(S) e^{+\beta V(R)} e^{\beta C_i}$$

$$p(S) = \sum_{N \text{ windows}} p_i S w_i$$

$$\frac{\eta_i e^{-\beta U_i(S)} e^{\beta C_i}}{\sum_{J=1}^N \text{windows} \eta_J e^{-\beta V_J(S)} e^{\beta C_J}}$$

For these terms we need to know what the unbiased $p(S)$ is, but that is what we are trying to solve. We need to know the ensemble average over the unbiased probability distribution.

$$e^{-\beta C_i} = \int e^{\beta V_i(S)} p(S) dS$$

We can guess that all $C_i = 0$ and then solve self-consistently until shifts of C_i are within some tolerance.

- (a) Related papers and books Look up **Umbrella integration** and **Thermodynamic integration**, where one can achieve this result analytically.

Original paper by Zwanzig in 1954

1993 Ben Roux: WHAM

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For the error of these one can do block averaging.

3. Adaptive potential bias

3.4 Michail Stamakatis: Statistical Mechanics

3.4.1 Introduction

Intensive variables don't depend on size of system (e.g. T, μ) Extensive variables do: (\mathcal{N}, V, S)

3.5 Useful definitions of Thermodynamic potentials

- Internal Energy:

- The capacity to do work and release heat.
- The energy contained within the system excluding kinetic energy.
- Equation:

$$U = \int (T dS - p dV + \sum_i \mu_i dN_i)$$

- ΔU is the total energy added to the system.
- Natural variables: $\{S, V, \{N_i\}\}$

- Helmholtz Free Energy:

- The energy at constant temperature and pressure.
- The capacity to do mechanical plus non-mechanical work
- Equation:

$$F = U - TS$$

- ΔF is the total work done on the system.
- Natural variables: $\{T, V, \{N_i\}\}$

- Gibbs Free Energy:

- The capacity to do non-mechanical work.
- The maximum amount of non-expansion work.
- The energy at constant temperature and pressure.
- Gibbs energy is the thermodynamic potential that is minimized when a system reaches chemical equilibrium at constant pressure and temperature.
- Equation:

$$G = U + pV - TS$$
- ΔG is the total non-mechanical work done on the system.
- Natural variables: $\{T, p, \{N_i\}\}$

- Enthalpy:

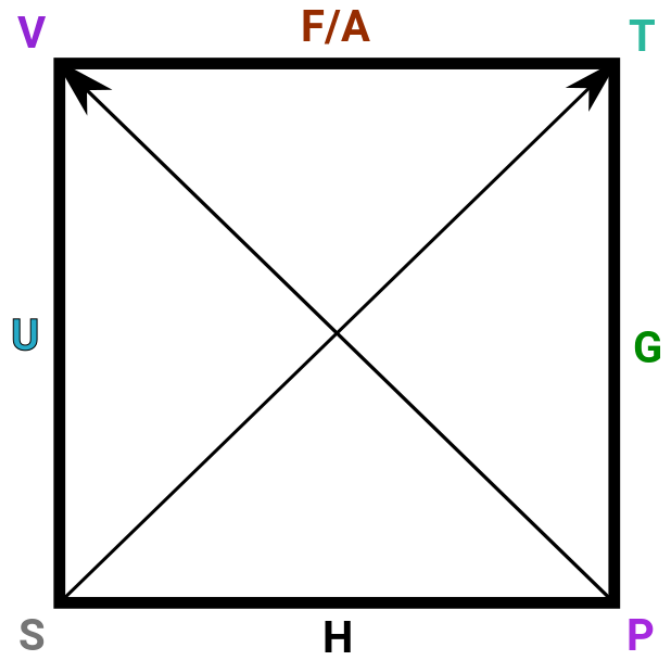
- The capacity to do non-mechanical work plus capacity to release heat.
- Equation:

$$H = U + pV$$
- ΔH is the total non-mechanical work and heat added to the system.
- Natural variables: $\{S, p, \{N_i\}\}$

3.5.1 Mnemonic Picture

Thermodynamic Mnemonic.

- Natural variables at corners of quantity in the middle.
- Direction of arrow determines if multiplicative quantity is positive or negative.



4 Useful Notes

4.1 Org-mode

(setq org-latex-create-formula-image-program 'dvipng)

4.2 Physics

4.2.1 Hartree-Fock

- Hartree-Fock is a method of calculating the energy of a configuration with exact exchange.
- This is done by essentially putting everything we don't know into the kinetic energy functional.
- Hamiltonian is split into contributions:

–

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{G}$$

– $\hat{G} = \hat{J} - \hat{K}$

– \hat{J} is the coulombic interaction:

–

$$\langle \mathbf{r} | \hat{J} | \mathbf{n} \rangle = \int \frac{\langle \mathbf{r} | n \rangle}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}$$

– So

$$E_{\text{H}} = \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

– This includes fictitious self-interaction of electron density.

– The Exchange functional removes this part, thus lowering the energy

- This method is used in Hybrid DFT. This corrects band gaps mainly. But there are also problems.

5 org-mode cheat sheet

- New TODO: M-<shift>-<ret>
- Done TODO: C-c C-t

- Links: `[[[]]] [link] then [description]`
- Open link: Move over cursor and do `C-c C-o`
- Link to local files:
 - Open file (`C-x C-f`) then do `C-c l`,
 - then go back to org file and do `C-c C-l` (e.g. `Upgradereportplusnotes`)
- To remove window in buffer `C-x 0`
- Overview of document `<shift>-<TAB>` to condense to titles.
- Can have global todo list
- `<s TAB` expands to a 'src' code block.
- `<l TAB` expands to a 'latex' code block. '
- If I want more help I can go to the org-mode manual

6 Bibliography

References