# things_to_do

November 27, 2018

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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 rmaxh is smaller or larger?
      - If rmaxh is is smaller (say rmaxh = 6.7 bohr) then we get the same results.

      ]]

      - Data: $a_{hcp}$ small rmaxh, $c_{hcp}$ small rmaxh, $e_{hcp}$ small rmaxh.
      - 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.

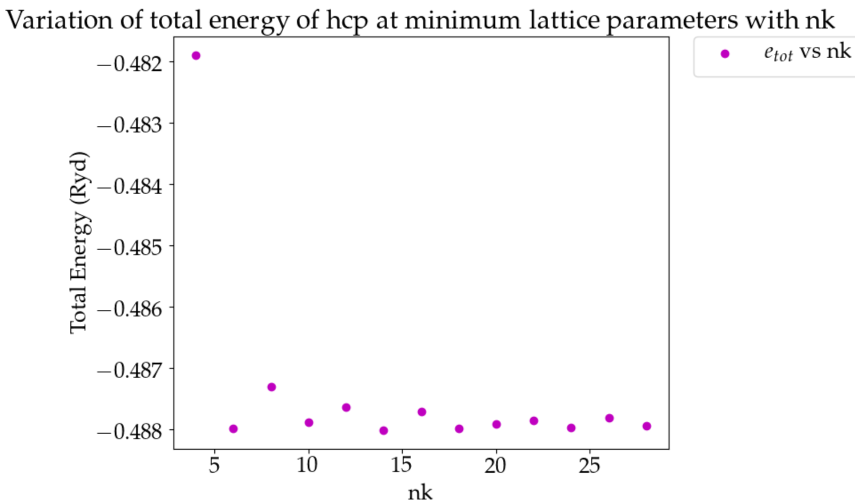


Figure 1: Variation of energy with k mesh.

#### 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
```

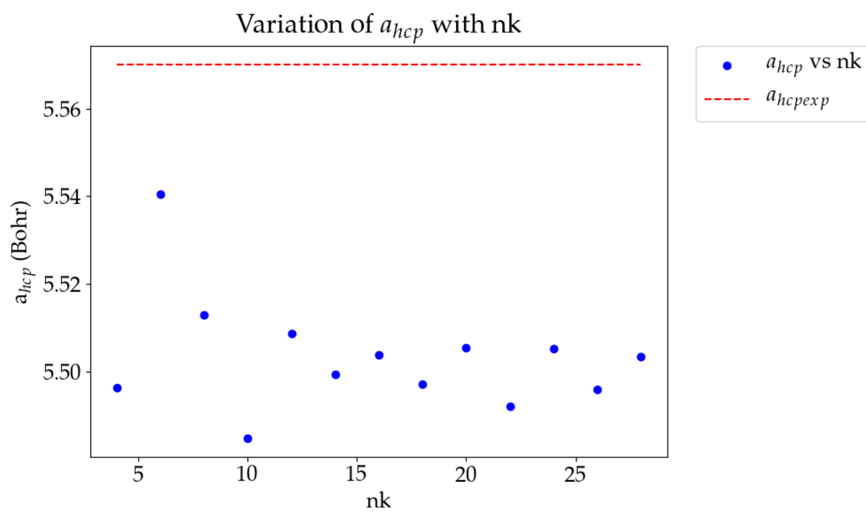


Figure 2: Variation of a hcp with k mesh.

### 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

### 1.5.1 TODO Summarise Stacking Faults and write review

### 1.5.2 TODO Write up the tight binding fitting of oxygen and an explanation for paramagnetism.

### 1.5.3 TODO Summarise dislocations and Oxygen interactions (review)

## 1.6 TODO Write summary of org-mode

## 1.7 DONE Look at the range of the bond integrals we have in Titanium graphically.

### 1.7.1 Pair potentials in tbe code

- Pair potential is constructed by makvpp.f.

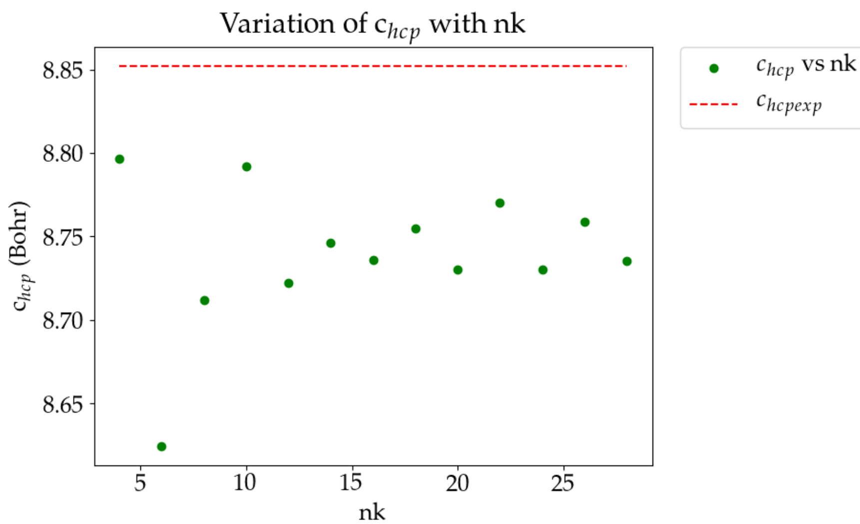


Figure 3: Variation of c hcp with k mesh.

- 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))
```

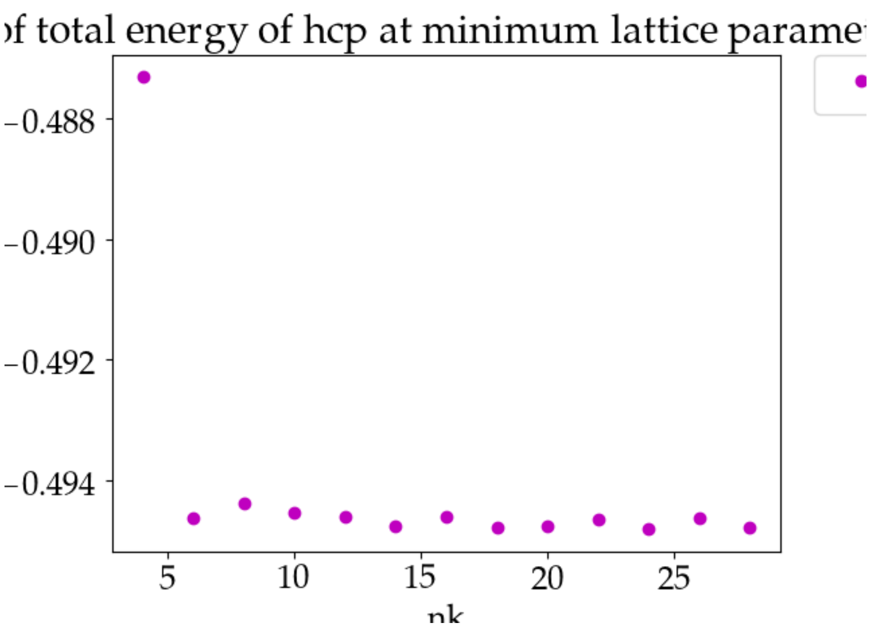


Figure 4: Variation of energy with k mesh.

```
        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

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

  *
$$P_2(x) = a(x - r1)^2 + b(x - r_1) + c$$

  *
$$a = \frac{1}{(r1 - r2)^5}\left\{\frac{1}{2}(r_1 - r_2)^2 f''(r_1) - 3(r_1 - r_2)f'(r_1) + 6f(r_1)\right\}$$

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

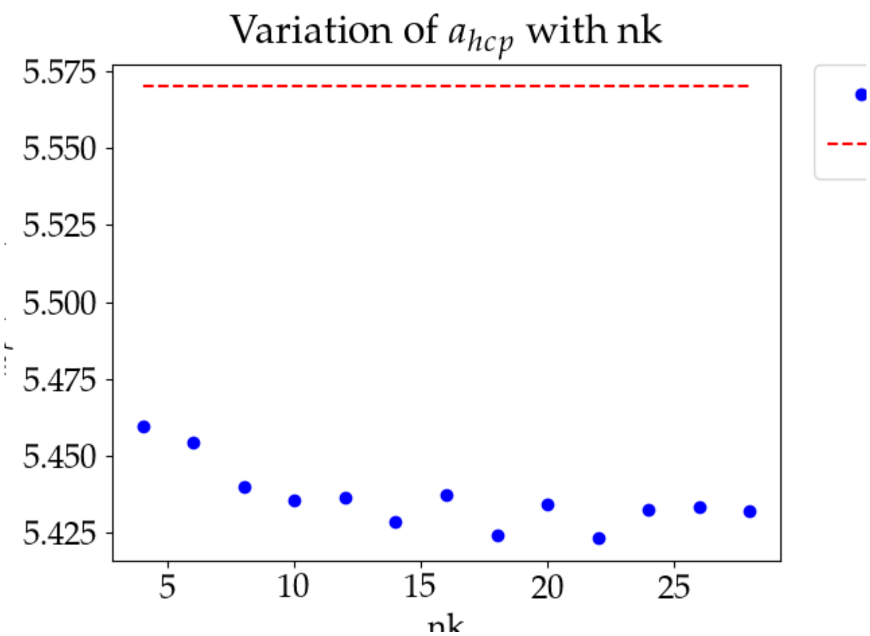


Figure 5: Variation of a hcp with k mesh.

* $$\frac{1}{(r_1 - r_2)^5}x$$
* $$c = \frac{f(r_1)}{(r_1 - r_2)^3}$$
* 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
```

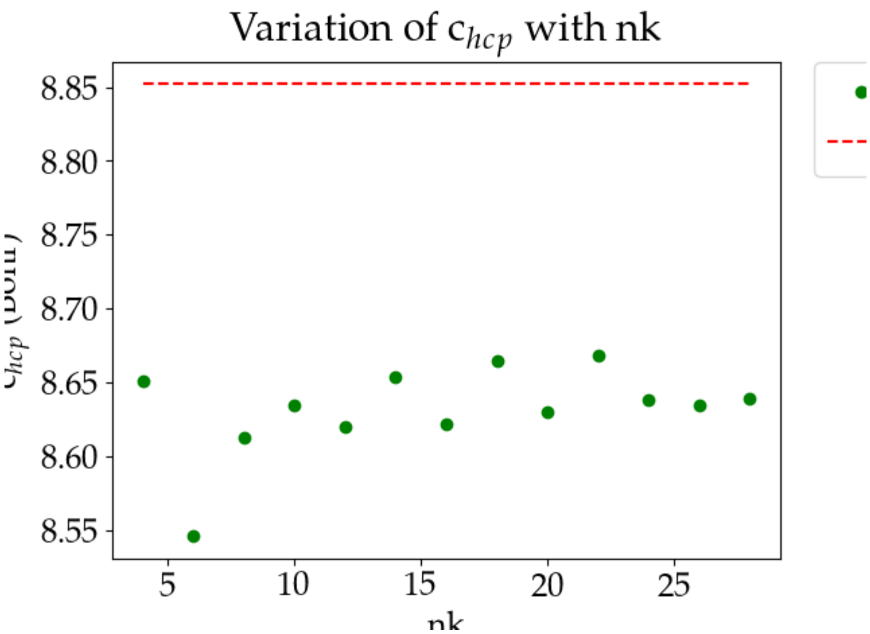


Figure 6: Variation of c hcp with k mesh.

#### 1.7.2 Bond integrals from tbe

- So bond integrals from titanium look like this, from this file plot$_{\text{bondintegrals}}$.py

### 1.8 DONE Investigate why rmaxh changes energy

- Variation of rmaxh does not change the energy
- Obviously the number of neighbours changes with rmaxh.
- Conclusion: rmaxh only determines what atoms are its neighbours.
- This is the file which investigates this: check$_{\text{rmaxhenergynumberneighbours}}$
- 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:

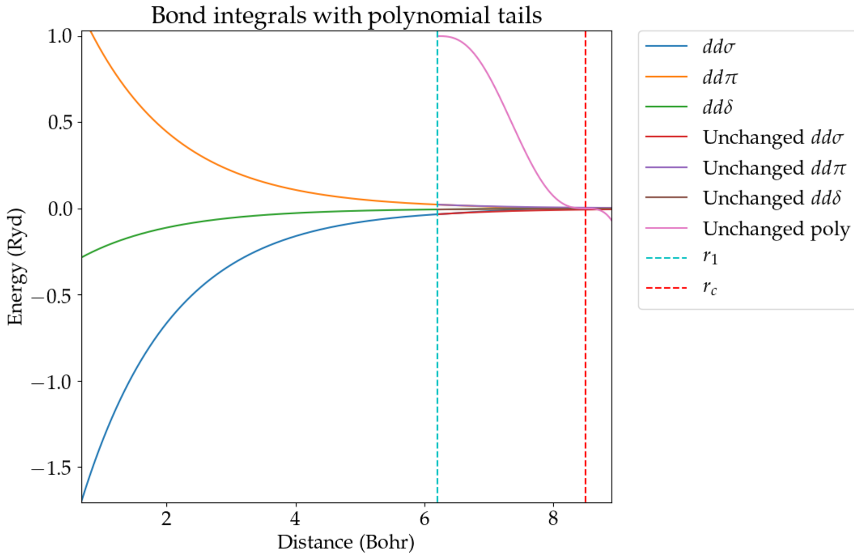


Figure 7: Bond integrals with multiplicative polynomial cutoffs.

### 1.9 DONE Show supercell of BOP working

# 2 General notes of codes.

## 2.1 Pair potentials in tbe code

### 2.1.1 How are they constructed?

- 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.
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xr1 = x - r1
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c = val*rr*rr
```

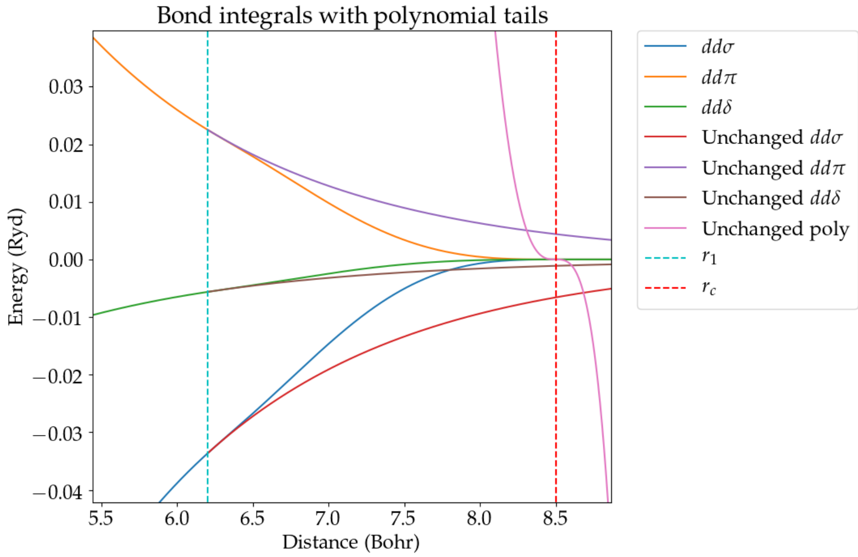


Figure 8: Bond integrals with multiplicative polynomial cutoffs: zoomed in.

```
      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
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  $$P_5(x) = (x - r_2)^3 P_2(x)$$
  *
  $$P_2(x) = a(x - r1)^2 + b(x - r_1) + c$$

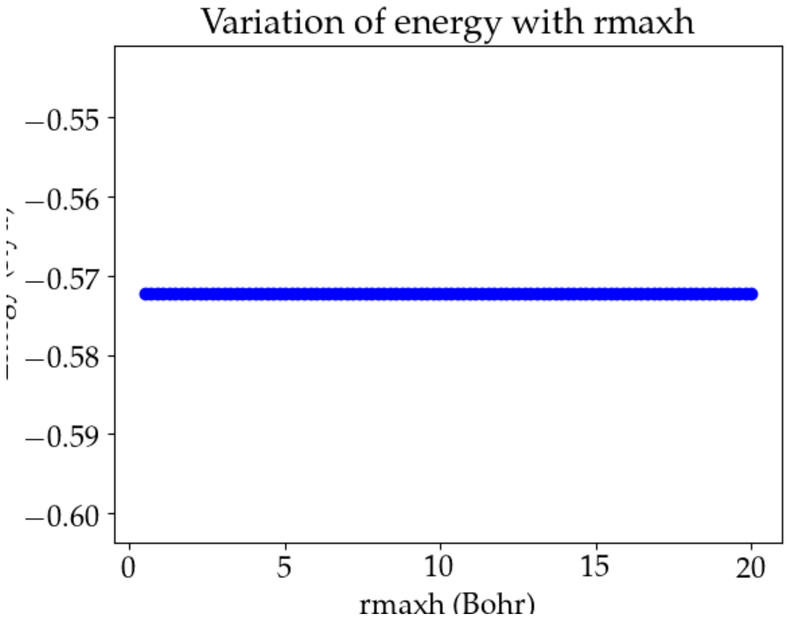


Figure 9: Variation of energy with change in rmaxh

  * $$a = \frac{1}{(r1-r2)^5}\{\frac{1}{2}(r_1-r_2)^2 f"(r_1) - 3(r_1-r_2)f'(r_1) + 6f(r_1)\}$$
  * $$b = \frac{1}{(r_1-r_2)^4}\{f'(r_1) * (r_1-r_2) - 3f(r_1)\}$$
  * $$\frac{1}{(r_1-r_2)^5}x$$
  * $$c = \frac{f(r_1)}{(r_1-r_2)^3}$$
  * Where $f(x)$ is the function that needs to be cut

- Current model has this

```
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     sss     sps     pps     ppp     sds     pds     pdp     dds     ddp     ddd
```

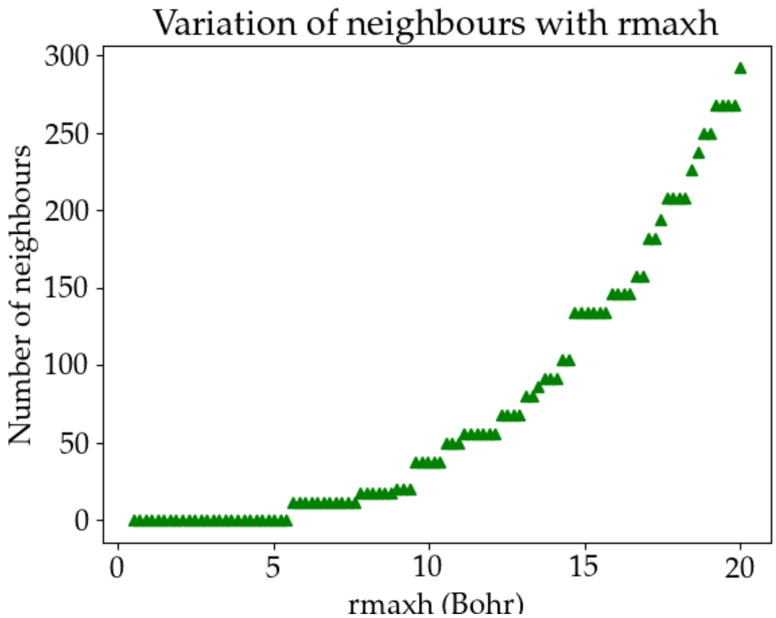


Figure 10: Variation of number of neighbours with change in rmaxh

```
coeff:   0.00   0.00   0.00   0.00   0.00   0.00   0.00  -2.75   1.84  -0.46
decay:   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.71   0.71   0.71
cutoff type 2 (multiplicative), 5th order polynomial, range [r1, rc]
  sss    sps    pps    ppp    sds    pds    pdp    dds    ddp    ddd
r1:      0.00   0.00   0.00   0.00   0.00   0.00   0.00   6.20   6.20   6.20
rc:      0.00   0.00   0.00   0.00   0.00   0.00   0.00   8.50   8.50   8.
```

#### 2.1.2 Bond Integrals: tbe

- So bond integrals from titanium look like this
- Bond integrals with multiplicative polynomial cutoffs.
- Bond integrals with multiplicative polynomial cutoffs: zoomed in.

### 2.2 Notes for the gamma surfaces

#### 2.2.1 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.

#### 2.2.2 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 positon e.g. 1d-8.

#### 2.2.3 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 ok 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 $n_{\mathrm{kx}}/\sqrt{3} \approx 17.3 \approx 17$
- 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 |

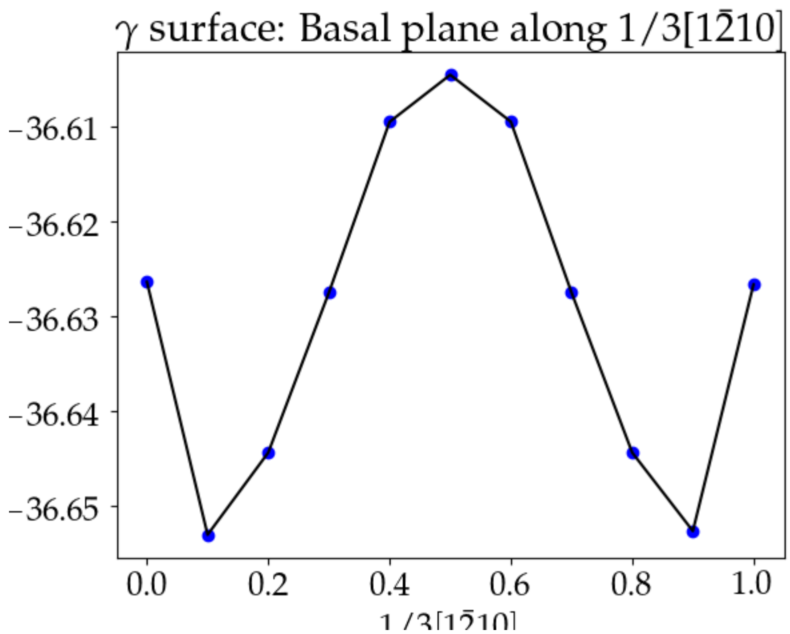
Less precise c/a below.

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 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 |

### 2.2.4 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: $basal_{energyplotting}$




#### 2.2.5 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 r0 therefore lies in the range **b** to 4**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 ($I_\mathrm{E}$) = (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 intrisic 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 involbe apsorption 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 $\gamma$-surfaces and stacking faults.

      - Comparison between central force embedded atom ineractions, N-body central force, N-body angular, empirical potentials, tight binding and DFT pseudopotential and DFT full electron calculations.
      - Cauchy pressures are deemed to due 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.

### 2.3 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 |
| $DeltaE_{Ohcp}$: | -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. |

## 2.4 Notes on Thermodynamics and Stability

### 2.4.1 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 $\Psi$ is minimum with respect to small virtual displacements of dions from equilibrium.
- Cauchy relations (at least in the cubic case) will be destroyed if non-central forces are included in the crystal potential.

### 2.4.2 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:
        - $C_{12}/C_{66}$
        - $C_{13}/C_{55}$
    - 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 dividiing by the bulk modulus: $C'_{ij} = C_{ij}/B$
    - It becomes easier to study trends as one is normlising 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.

## 2.5 Notes on Tight Binding and BOP Models

### 2.5.1 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 $_i$

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

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

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

### 2.6 DFT

Run:

- lmchk –getwsr ti
- Copy the old rmax into the R category in SPEC
- lmfa ti -vhcp=1
- Copy basp0 to basp
- Run lmf

## 3 Useful Notes

### 3.1 Org-mode

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

### 3.2 Physics

#### 3.2.1 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.

# 4 DFT Lectures UCL

## 4.1 David Bowler O(N) DFT

### 4.1.1 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

- $$E_{\mathrm{x}} = \int n(\mathbf{r})\epsilon_{\mathrm{xc}}[n(\mathbf{r})]F_{\mathrm{x}}(S)d\mathbf{r}$$
- $$E_{\mathrm{c}} = \int n[\epsilon_{\mathrm{c}} + H(n,S)]d\mathbf{r}$$
- 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
     $$V_{\mathrm{H}} = \int \frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}$$
   - The exchange term cancels the celf 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 hamilitonian 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.

## 4.2 Jochen Blumberger: Molecular dynamics

### 4.2.1 Introduction

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

### 4.2.2 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 $M_I \sim 1000 m_e$ 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
$$\hat{H}\Phi(\mathbf{R}) = E^0_{\mathbf{R}}\Phi(\mathbf{R})$$
  - Where $E^0_{\mathbf{R}}$ 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.

### 4.2.3 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.
     - $$\mathbf{R}_I(t+\delta t) = 2\mathbf{R}_I - \mathbf{R}_I(t-\delta t) + \frac{f_I(t)}{M_I}\delta t^3 \mathcal{O}(\delta t^4)$$
     - $$\dot{\mathbf{R}}_I(t) = \frac{1}{2\delta t}[\mathbf{R}_I(t+\delta t) - \mathbf{R}_I(t-\delta t)] + \mathcal{O}(\delta t^3)$$
     - 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 ($sim10^{-14}s^{-1}$, 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.
   - $$\mathbf{R}_I(t+\delta t) = \mathbf{R}_I(t) + \dot{\mathbf{R}}_I\delta t + \frac{f_I(t)}{M_I}\delta t^3 + \mathcal{O}(\delta t^3)$$
   - $$\dot{\mathbf{R}}_I(t+\delta t) = \dot{\mathbf{R}}_I(t) + \frac{1}{2M_I}[\mathbf{f}_I(t+\delta t) + \mathbf{R}_I(t)] + \mathcal{O}(\delta t^3)$$

3. How to calculate the forces

   - Use the Hellmann-Feynman theorem.
     - $$\mathbf{f}_I = \langle\psi^0_{\mathbf{R}}|\,\frac{\partial}{\partial\mathbf{R}_I}\hat{H}\,|\psi^0_{\mathbf{R}}\rangle$$

- This is derived using the parameter $\lambda$, assuming that the Hamiltonian depends on this lambda.

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)

## 4.3 Matteo Salvalglio: Enhanced Sampling

### 4.3.1 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

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

- 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.

### 4.3.2 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:

$$O = \langle O \rangle = \lim_{t \to \inf} \frac{1}{t} \int_0^t \mathrm{d}t O(x(t)),$$

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

### 4.3.3 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

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

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

  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

     $$\Delta F_{\mathrm{AB}} = -k_B T ln\{\frac{\int_B p(S)\mathrm{d}S}{\int_A p(S)\mathrm{d}S}\}$$

   - 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.

## 4.4 Useful definitions of Thermodynamic potentials

- Internal Energy:
  - The capacity to do work and release heat.
  - The energy contained withing the system excluding kinetic energy.
  - Equation:
$$U = \int (t\mathrm{d}S - p\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i)$$
  - $\Delta U$ 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:
$$F = U - TS$$
  - $\Delta F$ 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:
$$G = U + pV - TS$$

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

# 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. $\text{Upgrade}_{\text{report plus notes}}$)
- 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:
- If I want more help I can go to the org-mode manual