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Structural calculations and phase stability

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Overview of lecture

- Total Energy
  - Lattice constants
  - Pressure driven phase transitions
  - Bond energy, formation energy, surface …
- Forces
  - Hellman-Feynman theorem
- Stresses
- Elastic constants

Total Energy

Recap

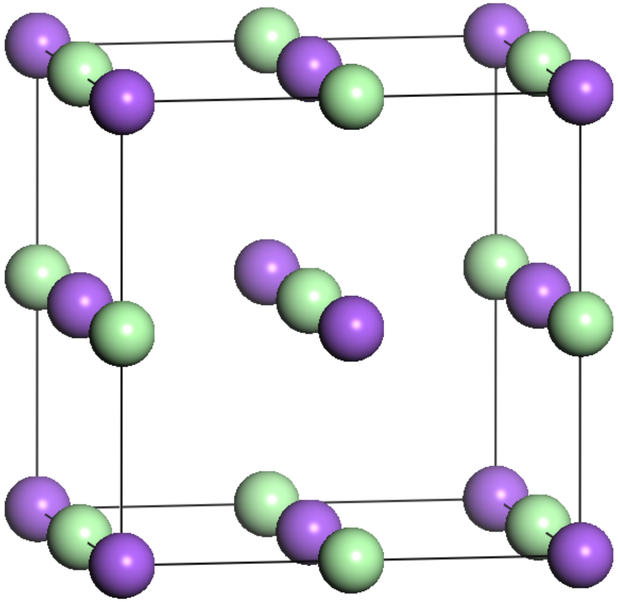
- Quantum Mechanics gives a complete description of materials chemistry & physics
  - QM of electrons and nuclei.
- Covalent, ionic, metallic and van der Waals bonding are all emergent properties of the QM behaviour of electrons.
- Born-Oppenheimer Approximation
  - Treat nuclei classically and assume electrons move adiabatically in a field of fixed ions.
  - QM electrons give interactions between atoms

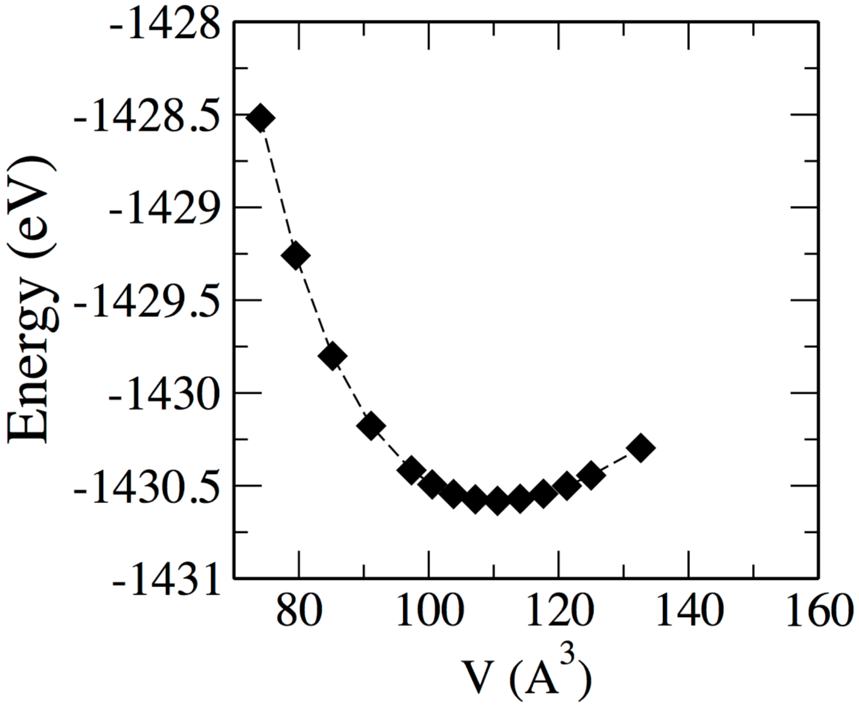
Total energy

- Primary computed property in DFT is the ground state energy.
  - All observables related to the *change* in energy when the system is perturbed.
- Crystal structure
  - Ion positions and lattice parameters that minimize the total energy.
- Phase stability
  - Phase with lowest E is most stable at T=0
- Elastic constants

Energy volume curves

- Consider a simple structure:
- The equilibrium CaO lattice parameter is given by the minimum energy:





Equation of State

- A popular EoS is the Birch-Murnaghan:

$$E(V) = E_0 + \frac{9V_0B_0}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^3 B_0' + \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^2 \left[6 - 4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right]\right\}$$

- Where the equilibrium volume is V_0 and the bulk modulus is given by

$$B_0 = -V \left.\frac{\partial P}{\partial V}\right|_{P=0}$$

- And the pressure derivative is $B_0' = \left.\frac{\partial B}{\partial P}\right|_{P=0}$

Phys. Rev **71** 809 (1947)

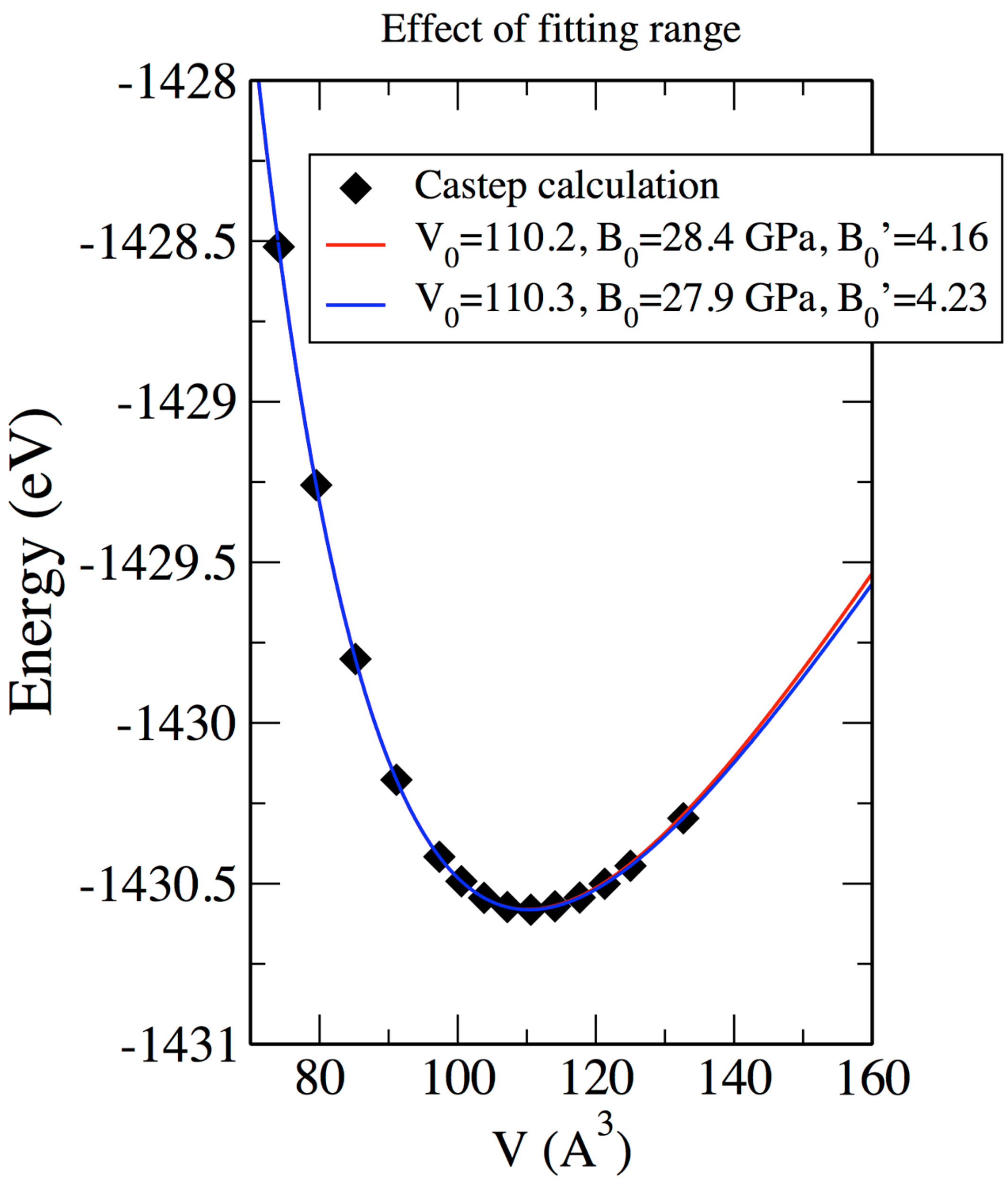
Birch-Murnaghan EoS

- The bulk modulus is a physical observable
- But two definitions
  - Can extract from fitting B-M EoS to compression data
  - Or from 2nd derivative as in ultrasound experiments

$$B_0 = -V_0 \frac{d^2 P}{dV^2}$$

  - And the results are not the same! Why?

B-M Fit



- Range of data changes fit!
- Experiment can only do $V<=V_0$ but calculation can do both
- Must use same (or similar) range of V as in experiment to get comparable B_0

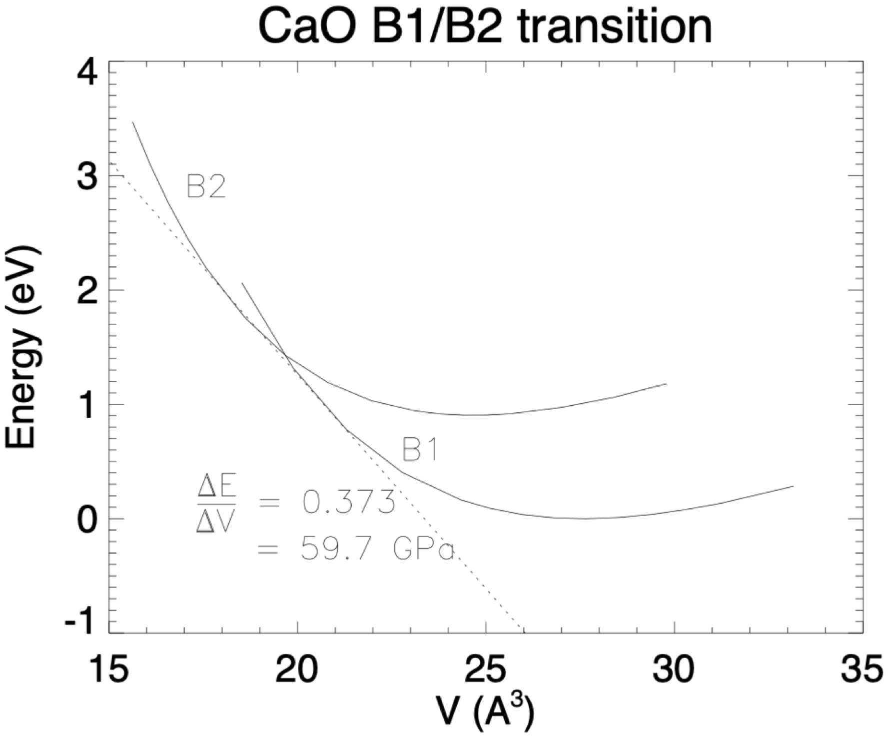
First order phase transitions

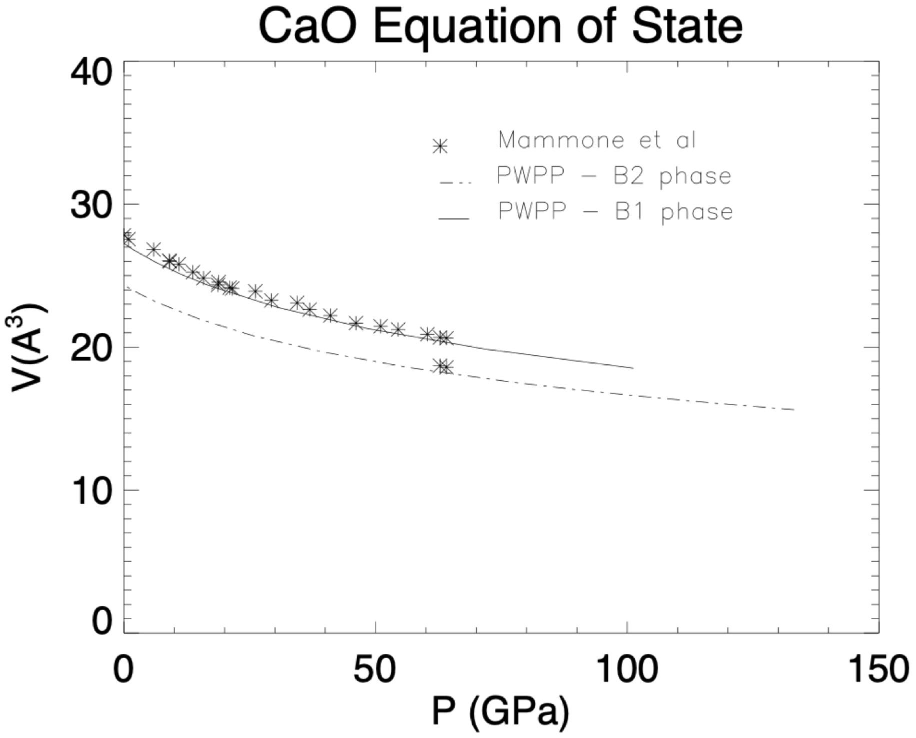
- A structure will change phase to the one of lowest free energy
- Phase equilibrium happens if:
  - Pressure of both phases are equal
  - Enthalpy of both phases are equal:

$$E_2 - E_1 = P(V_2 - V_1)$$

  - Can use gradient of common tangent to get transition pressure …

CaO Phase Transition

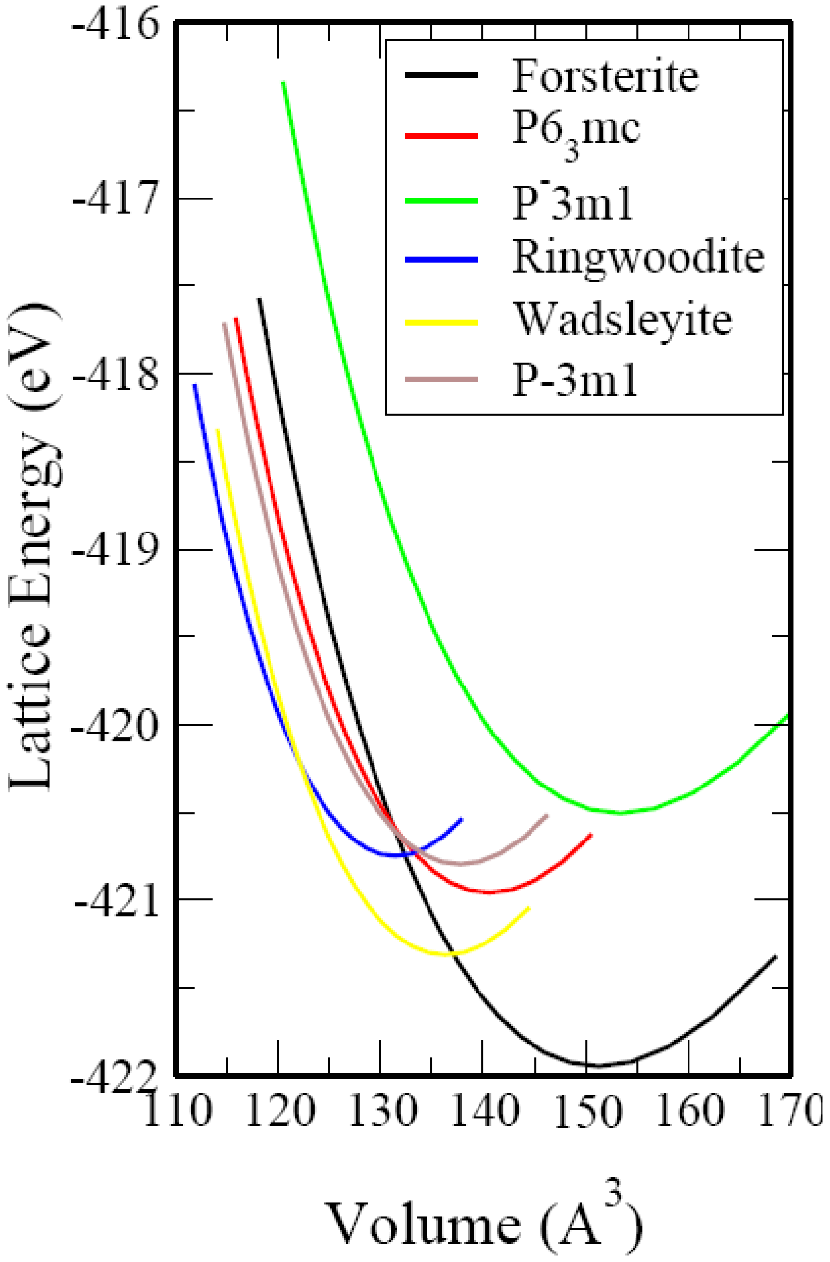




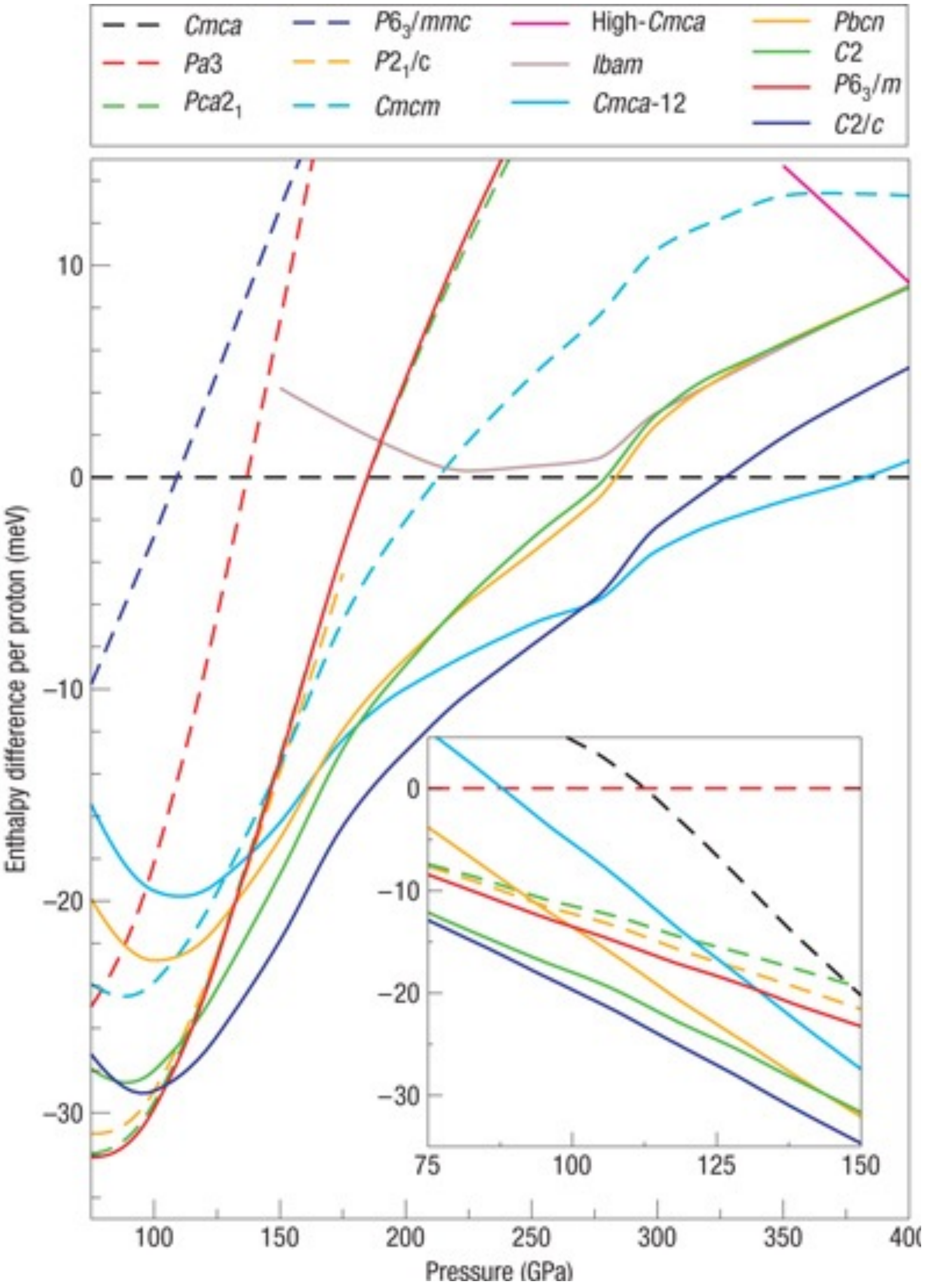
- Or can plot enthalpy *H* vs pressure *P* and see which phase has lowest *H* at given *P*
- Requires accurate *P* calculation …

More complex, e.g. TiO_2

- Which phase is most stable?
  - calculate E(V) curve
  - Forsterite is most stable of al the phases considered
  - then Wadsleyite and then Ringwoodite as increase pressure
- Limited to set of considered structures
  - What if miss something?
  - Active research topic …

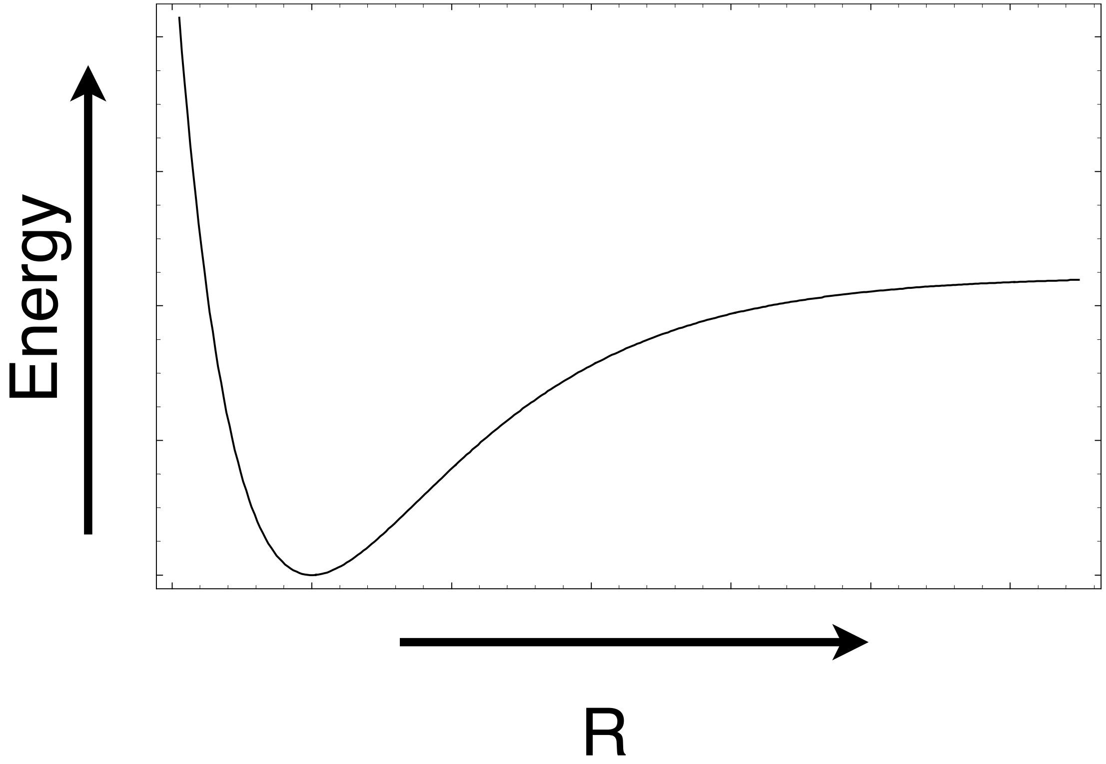


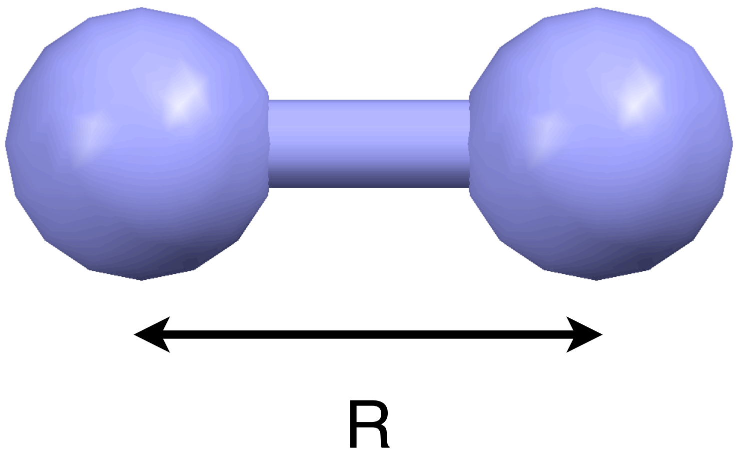
- High pressure Hydrogen
- Plot ΔH wrt *Cmca* phase
- Solid lines are new structures, dashed had been already considered by others



Bonds

- Atoms form bonds in solids in molecules
- Energy varies with length of bond:





- Hence min energy = equilibrium bond length

Dissociation Energy

- If we stretch a bond too much it will break
  - Energy required is the *dissociation energy*, i.e. ΔH = E(molecule) - sum E(fragments)
  - Example: methane CH_4
    - dissociation energy = E(CH_4) - E(CH_3) - E(H)
    - Covalent bonds are strong – typically 1-5 eV
    - Environment dependent
- Always requires energy => endothermic
  - H_3C-H bond is ~4.5 eV as bond is short
  - N_2 triple bond is VERY strong = 9.8 eV

Bond Energy

- Average dissociation energy over all bonds in a molecule is the *bond energy*
  - More transferable
  - Example: methane CH_4
    - bond energy = $\frac{1}{4}*(E(CH_4)-E(C)-4E(H))$
- NB long bonds are weak
  - BE of H-H = 4.5 eV, length = 0.74 Å
  - BE of H-C = 4.3 eV, length = 1.09 Å
  - BE of H-Si = 3.3 eV, length = 1.48 Å
  - BE of Si-Si = 2.3 eV, length = 2.33 Å

Cohesive energy

- For solids or liquids
  - The energy required to break all the bonds between the basic units (atoms or molecules) of the material
  - i.e. the intra-molecular bonds
- Example: silicon
  - Cohesive energy = $1/n *(E(Si_n) – n*E(Si))$
- Example: water ~ 0.4 eV/molecule
  - Relates to boiling point of water – not dissociating water into H_2 and ½ O_2 !

Defect formation energy

- What about defects? Simplest is the point vacancy – a single missing atom …
- Neutral vacancy in an elemental solid:

$$E_V = E_{N-1} - \left(\frac{N-1}{N}\right) E_N$$

- Need to consider effect of relaxation around the vacancy – inward or outward?
- Might also be symmetry breaking
  - e.g. Jahn-Teller effect

Defect formation energy

- More general, for charged defects in non-elemental system:

$$E_{\text{form}} = G_{\text{defect}} - G_{\text{ideal}} = H_{\text{defect}} - H_{\text{ideal}} + \sum_j n_j \mu_j^{\text{removed}} - \sum_j n_j \mu_j^{\text{added}} - n_{\text{e}} \mu_{\text{e}}$$

  - Includes change in free energy and change in chemical potential and charge transfer
- Depends on reservoir
  - Where do the defect atoms go/come from?
- Neglects change in entropy

Chemical potential

- For an elemental solid, chemical potential μ is the energy of gas phase
- For an compound solid, depends on chemical bonds present
  - E.g. quartz (SiO_2):

$$\mu_{\mathrm{SiO_2}} = \mu_{\mathrm{Si}} + \mu_{\mathrm{O_2}} = \mu^*_{\mathrm{Si}} + \mu^*_{\mathrm{O_2}} + \Delta H_{\mathrm{SiO_2}}$$

$$\mu^*_{\mathrm{Si}} + \Delta H_{\mathrm{SiO_2}} \leqslant \mu_{\mathrm{Si}} \leqslant \mu^*_{\mathrm{Si}}$$

$$\tfrac{1}{2}\mu^*_{\mathrm{O_2}} + \tfrac{1}{2}\Delta H_{\mathrm{SiO_2}} \leqslant \mu_{\mathrm{O}} \leqslant \tfrac{1}{2}\mu^*_{\mathrm{O_2}}$$

where μ^*_{Si} is chem pot of gas-phase Si, and $\mu^*_{\mathrm{O_2}}$ is the chem pot of diatomic gas-phase O_2

Surfaces

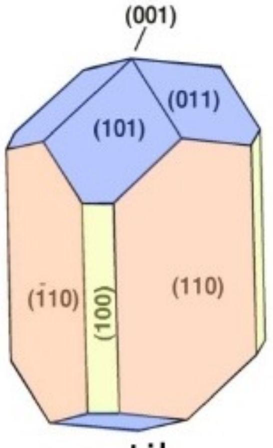
- As well as studying bulk materials and defects, can also study surfaces
- Surface energy γ is the energy required to form a surface:

$$\gamma = \frac{1}{2A}\left(E_{surface} - k * E_{bulk}\right)$$

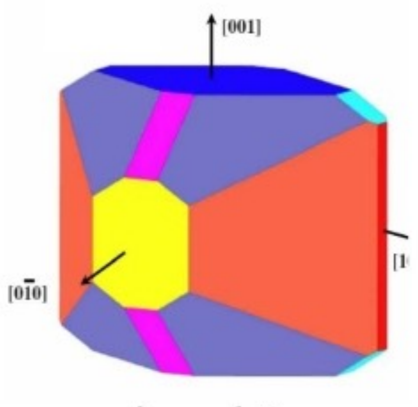
  - Where the surface calculation contains 2 surfaces separated by *k* planes of atoms
  - And E_{bulk} is the energy in bulk of 1 plane
  - And *A* is the area of the surface created
- Can also be measured directly in expt

Wulff construction

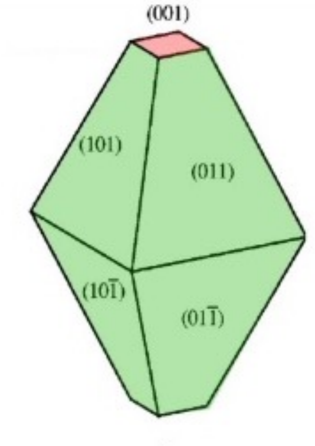
- The equilibrium shape of a crystal or nanoparticle is given by min Gibbs free energy
- Surface Gibbs free energy is $\Delta G = \sum_j \gamma_j A_j$
  - Variational problem – minimize ΔG subject to fixed volume constraint
  - Hence surface with lowest γ will dominate
  - e.g. TiO_2



rutile
$\langle\gamma\rangle = 1.1\ J/m^2$



brookite
$\langle\gamma\rangle = 0.7\ J/m^2$

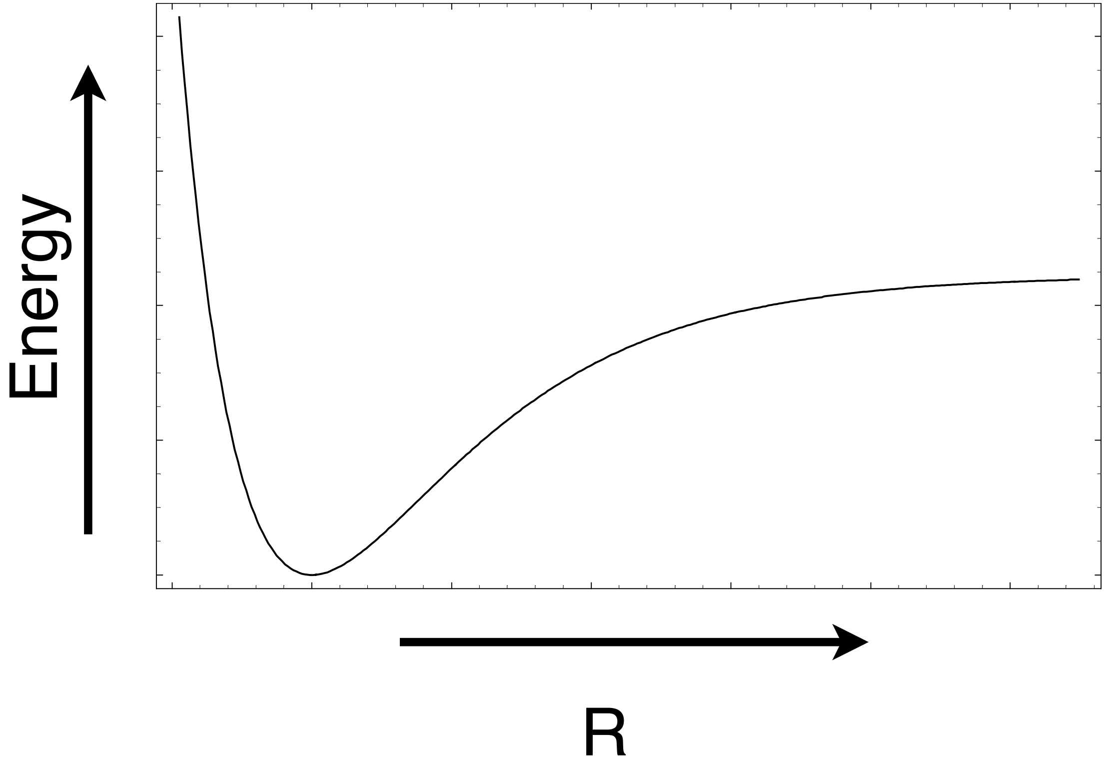


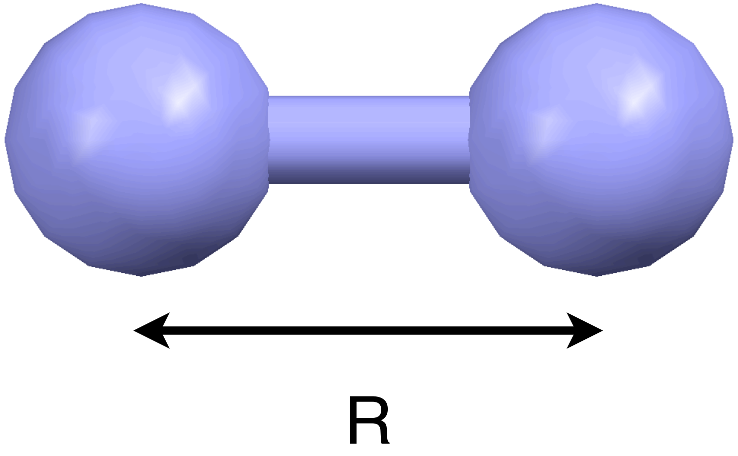
anatase
$\langle\gamma\rangle = 0.5\ J/m^2$

Forces

Forces

- For a given set of atomic positions the atoms will feel a force if not at equilibrium:





- Rule of thumb: F>1.0 eV/Å is a large force.

Forces and Stresses

- Minimum energy configuration corresponds to zero force
  - Using forces to find the minimum is much more efficient than just using energy alone
- Minimum enthalpy corresponds to zero force and stress
  - Can therefore minimise enthalpy w.r.t. supercell shape due to internal stress and external pressure
  - Can minimize under external pressure to find new structures

QM Forces

- Classically we have the force **F** at position **R** is determined from the potential energy as

$$\mathbf{F} = -\nabla_{\mathbf{R}} U(\mathbf{R})$$

- Quantum mechanically we therefore expect

$$\mathbf{F} = -\nabla_{\mathbf{R}} \langle E \rangle$$

where

$$\langle E \rangle = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Stresses

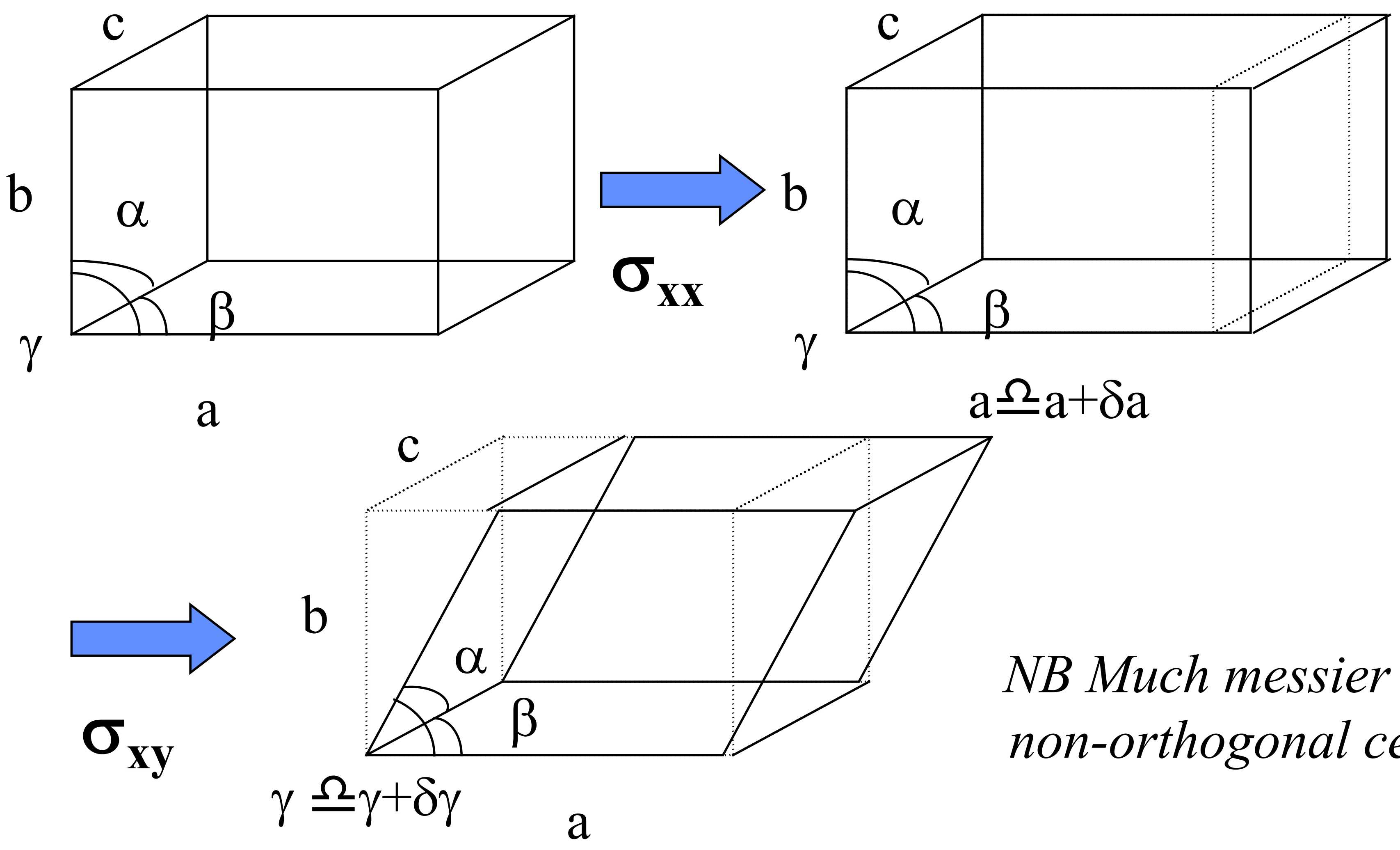
Stress

- Whilst force is a simple 3-vector, stress is a rank-2 tensor

$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yx} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

- Symmetry reduces this to 6 independent components:
  - Diagonal = σ_{xx}, σ_{yy}, σ_{zz} = compression
  - Off-diagonal = σ_{xy}, σ_{yz}, σ_{zx} = shear
- Convention: $\mathbf{P}_{ext} + \boldsymbol{\sigma} = 0$ at equilibrium
  - i.e. P>0 = compression, $P_{int} = 1/3\ \mathrm{Tr}(\boldsymbol{\sigma})$

Stress in action



NB Much messier if non-orthogonal cell

QM Stresses

- If we write the three unit cell vectors **a**, **b**, **c** as the columns of a matrix **h** then the effect of an applied strain $\boldsymbol{\varepsilon}$ is to change the shape of the unit cell:

$$\mathbf{h}' = \left(\mathbf{I} + \boldsymbol{\varepsilon}\right)\mathbf{h}$$

- We then have the stress tensor $\boldsymbol{\sigma}$ related to the strain tensor $\boldsymbol{\varepsilon}$ by:

$$\sigma_{\alpha\beta} = \frac{1}{V}\frac{\partial E}{\partial \varepsilon_{\alpha\beta}}$$

where V is the volume of the unit cell.

Elastic Constants

Elastic Constants

- In 1D you know $E = E_0 + \frac{1}{2}k\left(x - x_0\right)^2$

  where k = elastic constant

- or in terms of dimensionless strain:

$$E = E_0 + \frac{L}{2}k\delta^2$$

- In 3D, we have 4th rank elastic constants tensor but can write as 6x6 using Voigt:

$$E(\epsilon) = E_0 + \frac{V}{2}\sum_{ij}^{6} C_{ij}\epsilon_i\epsilon_j + O(3)$$

- which has max 21 unique components

Simple elastic constants

- For certain high-symmetry crystals there are only a few distinct components to c_{ij}
  - Hence can efficiently calculate with the appropriate minimal pattern of strains
  - E.g. in a cubic crystal there are only 3 distinct terms: c_{11}, c_{12} and c_{44}
  - E.g. can choose strain to just study c_{44}:

$$\epsilon = \frac{1}{2}\begin{bmatrix} 0 & \delta & \delta \\ \delta & 0 & \delta \\ \delta & \delta & 0 \end{bmatrix} \qquad E = E_0 + \frac{3V}{2} C_{44}\delta^2 + O(3)$$

Summary

Summary

- Total energy is VERY useful
  - Changes can determine phase stability, lattice parameters, bond energies, defect energies, surface energies, etc.
- Can also calculate derivatives
  - E.g. forces (change wrt ionic positions)
  - E.g. stress (change wrt cell parameters)
  - E.g. elastic constants (2nd order strain derivative)

Useful References

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