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Introduction to CASTEP & Density Functional Theory

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- What is DFT?

- What is CASTEP?

- What can it do for my research?

- Summary

What is DFT?

- # Density Functional Theory
  - ## An alternative view of Quantum Mechanics
  - ## Uses the electronic charge density of a material as the key ingredient
    - ### No need for wavefunctions
  - ## Intended to make electronic structure calculations of real materials a practicality
    - ### What should that be tricky?

- The 1-particle Schrödinger equation is:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \hat{V} \right) \Psi\left(\mathbf{r}, t\right) = i\hbar\frac{\partial \Psi\left(\mathbf{r}, t\right)}{\partial t}$$

- So all we need to do is solve that for a real material – how hard can it be?

- A real material contains M nuclei and N electrons and so Schrödinger equation is:

$$\left\{ -\frac{\hbar^2}{2} \left(\frac{\nabla_{n1}^2}{m_1} + ... + \frac{\nabla_{nM}^2}{m_M}, \frac{\nabla_{e1}^2}{m} + ... + \frac{\nabla_{eN}^2}{m} \right) \right.$$

$$\left. + \hat{V}(\mathbf{R}_1, ..., \mathbf{R}_M, \mathbf{r}_1, ..., \mathbf{r}_N, t) \right\} \Psi(\mathbf{R}_1, ..., \mathbf{R}_M, \mathbf{r}_1, ..., \mathbf{r}_N, t)$$

$$= i\hbar \frac{\partial \Psi(\mathbf{R}_1, ..., \mathbf{R}_M, \mathbf{r}_1, ..., \mathbf{r}_N, t)}{\partial t}$$

For a few grams of material we typically have $M \sim 10^{23}$ and $N \sim 10^{24}$ …

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- Assume only need QM for electrons

  - Usually OK as $m_e \ll m_p$

  - Can break down for light atoms and/or low T

  - And so nuclei appear static to electrons

  - So no need for time dependence

  - This is known as the Born-Oppenheimer approximation

$$\Psi\left(\mathbf{R}_1, ..., \mathbf{R}_M, \mathbf{r}_1, ..., \mathbf{r}_N, t\right) \longrightarrow \psi\left(\mathbf{r}_1, ..., \mathbf{r}_N\right)$$

- ## Focus on the ground state
  - ### Often dominates everyday properties
  - ### Not true for optical properties

- ## The wavefunction is not experimentally measurable – only the density …

- ## Density Functional Theory
  - ### Hohenberg-Kohn Theorem 1964
  - ### Kohn-Sham Equations 1965
  - ### Nobel prize for Kohn 1998

- # H-K Theorem

  - ## The groundstate energy *E* ONLY depends on the electron density $\rho(\mathbf{r})$

  - ## And the mapping is unique

- # K-S Equations

  - ## The groundstate energy *E* and density $\rho(\mathbf{r})$ of electrons are exactly the same as those of *non-interacting* particles, iff we include an extra potential – the *exchange-correlation potential* = V_{xc}

- Converts the many-body Schrödinger equation for *N* electrons into *N* equations each with 1 quasi-particle:

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V\left[\rho\right](\mathbf{r}) + V_{xc}\left[\rho\right](\mathbf{r}) \right\} \psi_b(\mathbf{r}) = \epsilon_b \psi_b(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_{j=1}^{N} |\psi_b(\mathbf{r})|^2$$

- and $V\left[\rho\right]$ and $V_{xc}\left[\rho\right]$ are density *functionals*

  NB exact form of V_{xc} is unknown –
  but we do have good approximations

- But we still have $N\sim10^{24}$ so is it impossible to solve DFT for real materials?

- In a solid, most materials form a regular pattern – can make up out of repeating *unit cells* – so we can exploit *periodicity* …
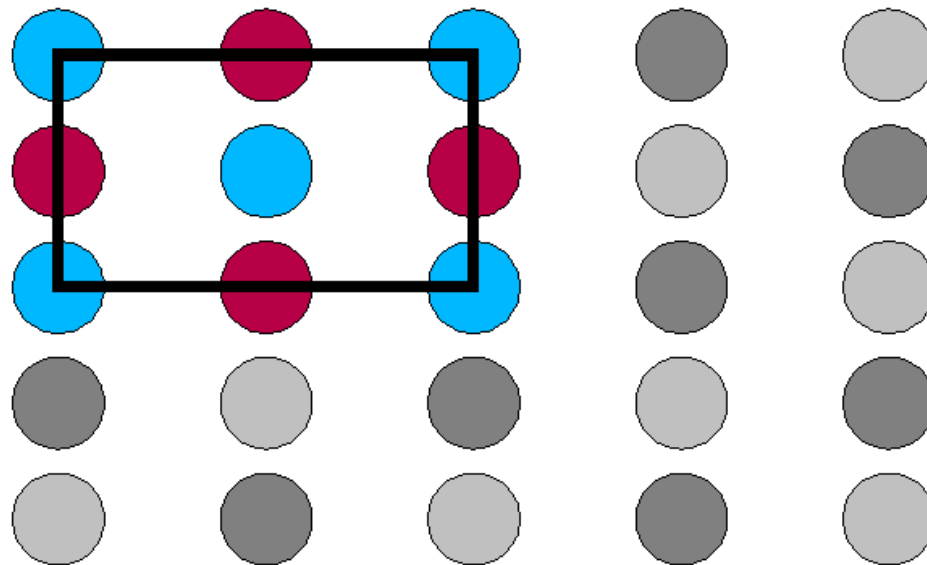
- A fundamental theorem of condensed matter physics

- If the nuclei are arranged periodically then the potential must be periodic:

$$V(\mathbf{r} + \mathbf{L}) = V(\mathbf{r})$$

- And so the wavefunction must be 'quasi-periodic':

$$\psi_k(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} u_k(\mathbf{r})$$

- where $u_k(\mathbf{r} + \mathbf{L}) = u_k(\mathbf{r})$ is periodic and $e^{i\mathbf{k}.\mathbf{r}}$ is an arbitrary phase factor.

- ## So now we only have to solve the K-S equations in a single unit cell

  - ### Hence $N \sim 10^2$ not 10^{24} …

  - ### Hence calculate energy per unit cell, etc

- ## Although in fact we are simulating an infinite number of electrons …

- ## And can use *supercell* approach to handle *aperiodic* systems e.g. molecules, surfaces, interfaces, grain boundaries, etc.

What is CASTEP?

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CaS$_2$TeP

2eV indirect

band gap
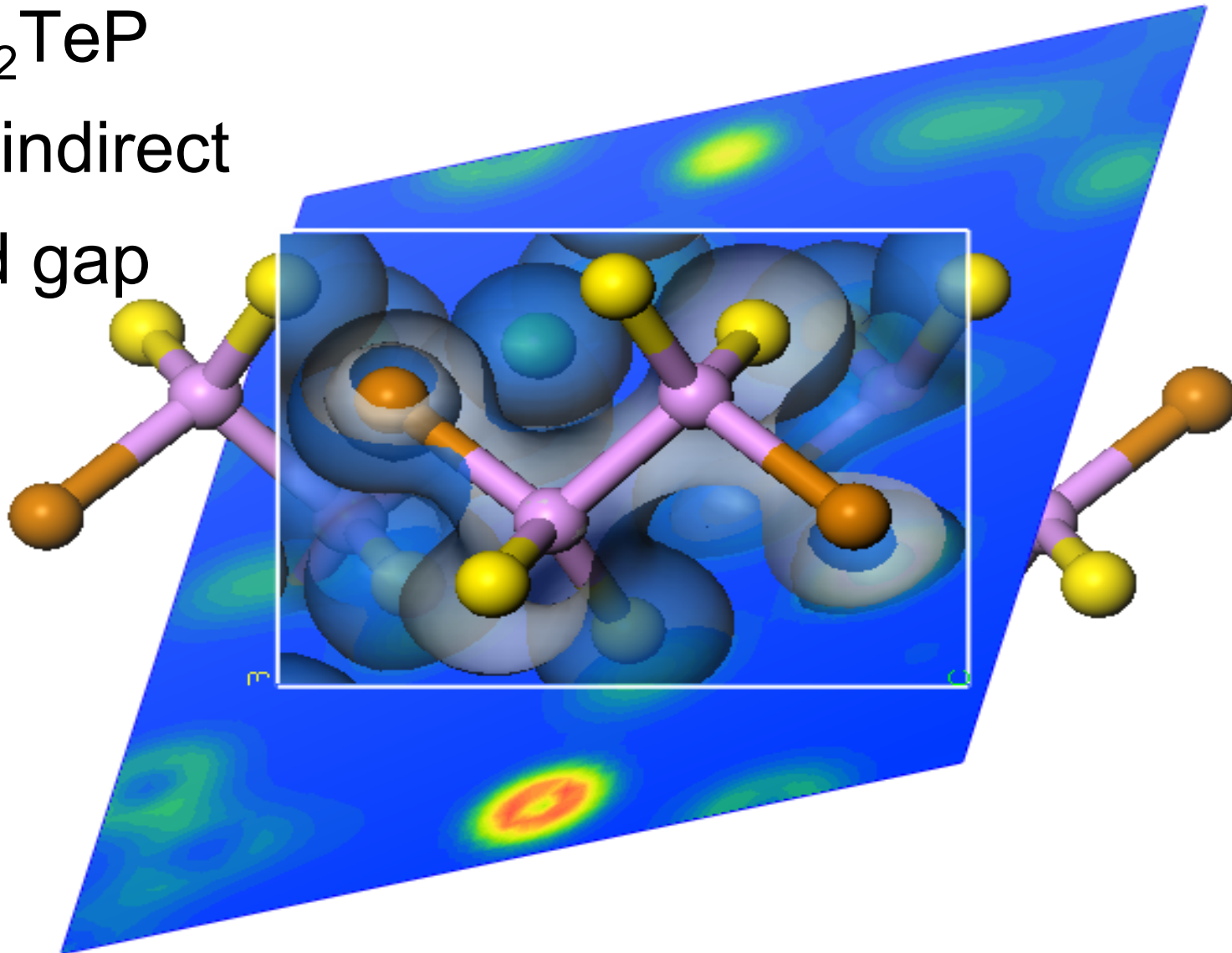
- # CASTEP is a general-purpose DFT code

  - ## uses plane-wave basis set (position independent, easy to improve accuracy)

  - ## use pseudopotentials (replaces nuclei and inner electrons with pseudo-ion)

  - ## is parallel (can run on single core PC or largest supercomputer)

  - ## can calculate wide range of properties …

- Total energies
  - forces and stresses, with LDA/GGA/sX/hybrid/LDA+U/vdW etc.
- Electronic structure
  - electronic charge, potential, band structure, DOS, atomic populations
- Geometry Optimisation
  - atomic positions, cell parameters, external pressure/stress
- Molecular dynamics
  - finite temperature, zero-point and non-equilibrium properties
- Transition state searches
  - chemical reaction pathways, diffusion barriers
- Phonons
  - perturbation theory, finite differences
- Electric field response
  - polarisability, dielectric constants, Born charges, LO/TO splitting
- Magnetic Response
  - NMR, Chemical shifts, electric field gradients, hyperfine constants, etc.
- ELNES, EELS, Raman, IR, Wannier Functions, and more …

- CASTEP is developed by a core team of UK academics + collaborators:
    - Stewart Clark (University of Durham)
    - Phil Hasnip (University of York)
    - Chris Pickard (University of Cambridge)
    - Matt Probert (University of York)
    - Keith Refson (Royal Holloway London)
    - Jonathan Yates (University of Oxford)
- Plus many PhD students + postdocs

- Each developer is responsible for a different part of the code - principally:
  - Stewart Clark = XC functionals
  - Phil Hasnip = ground state energy
  - Chris Pickard = pseudopotentials
  - Matt Probert = geometry optimisation + MD
  - Keith Refson = phonons
  - Jonathan Yates = NMR
- Plus other areas too!

What can it do for my research?

- Can use CASTEP for a purely theoretical study

  - To elucidate underlying mechanism of a reaction or process, or to study materials under extreme conditions, or …

- Or in collaboration with experimentalists

  - To help interpret experiments, predict spectra, or ...

- Or …

$NaCaB_5O_7(OH)_4.$
$3(H_2O)$
{z=4}
124 ions
512 electrons
$E_{gap} \sim 5$ eV

Basic energy
minimization
took 36 secs
on 72 cores …

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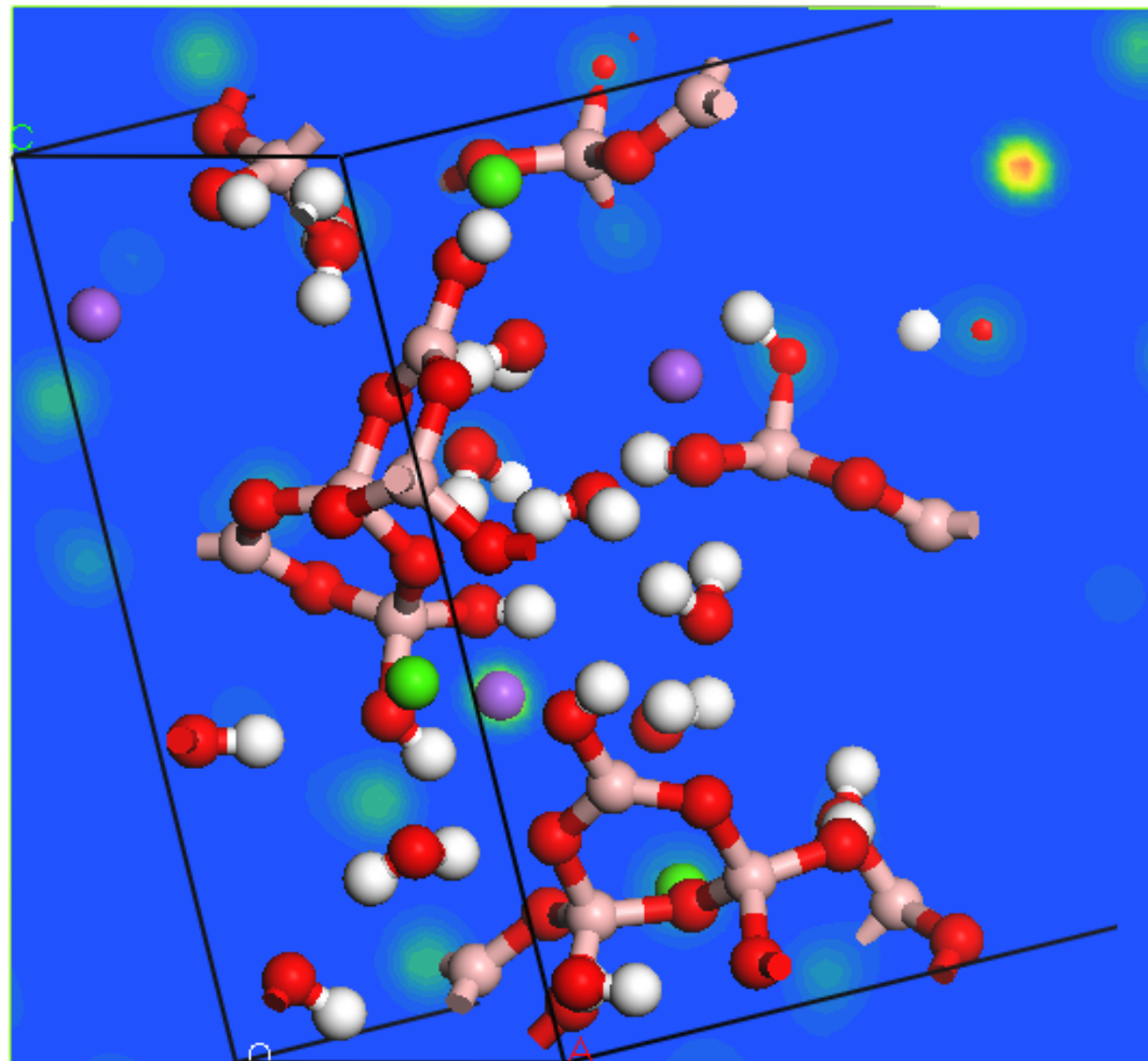
Water-Hydroxyl Overlayers on Metal Surfaces

Phys. Rev. Lett. **104**, 066102 (2010)

Xin-Zheng Li, Matt Probert, Ali Alavi, and Angelos Michaelides

- In many systems, the initial wetting layer is not pure water, but a water-hydroxyl mix

    - Bond lengths/angles unusual due to "pinning" with hydrogen-bonds formed to surface atoms

- Transition metal surfaces have been well-characterised

    - Pt(111) has large lattice constant and so inter-molecule distance ~ 2.83 Å

    - Ni(111) has much smaller distance ~2.50 Å

- ## In bulk ice have typical O-O distance ~ 2.8Å

- ## At high pressures (>70 GPa) ice has typical O-O distance of ~2.3 Å

  - ### No longer a molecular crystal

  - ### Have delocalised protons between O nuclei

- ## Low T (160 K) measurements of hydrogen diffusion on metal surfaces suggests that quantum tunnelling important

 - ### Hence need full QM treatment for hydrogen!

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- *ab initio* Molecular Dynamics
  - Use classical mechanics to move the atoms
    - Born-Oppenheimer approximation decouples nucleus and electrons and have electrons always relaxed onto the instantaneous B-O surface
  - but using forces and stresses derived from the electronic wavefunction – hence *ab initio* MD
  - can use to study dynamical properties or to simulate a statistical ensemble (e.g. NVE, NVT, NPH or NPT) with various thermostats and/or barostats, etc.

- But the nucleus is always treated classically
  - hence no quantum fluctuations, tunneling, zero point motion, etc.

- ## Use Feynman Path Integral formulation of Quantum Mechanics for the nucleus

  - ### now includes ZPM etc

  - ### important for light defects and/or low temperatures

  - ### "beads on springs" view with imaginary time axis

  - ### computationally expensive!

 - ### Use task-farming – one value of $i\tau$ per farm
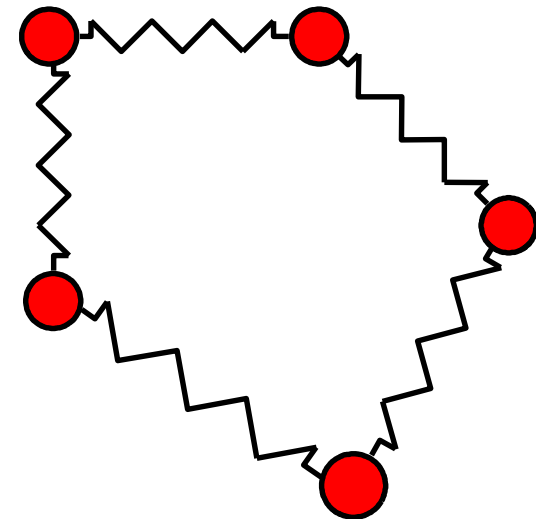
Path integral view of a single quantum particle.

Nickel PIMD Movie

Platinum PIMD Movie
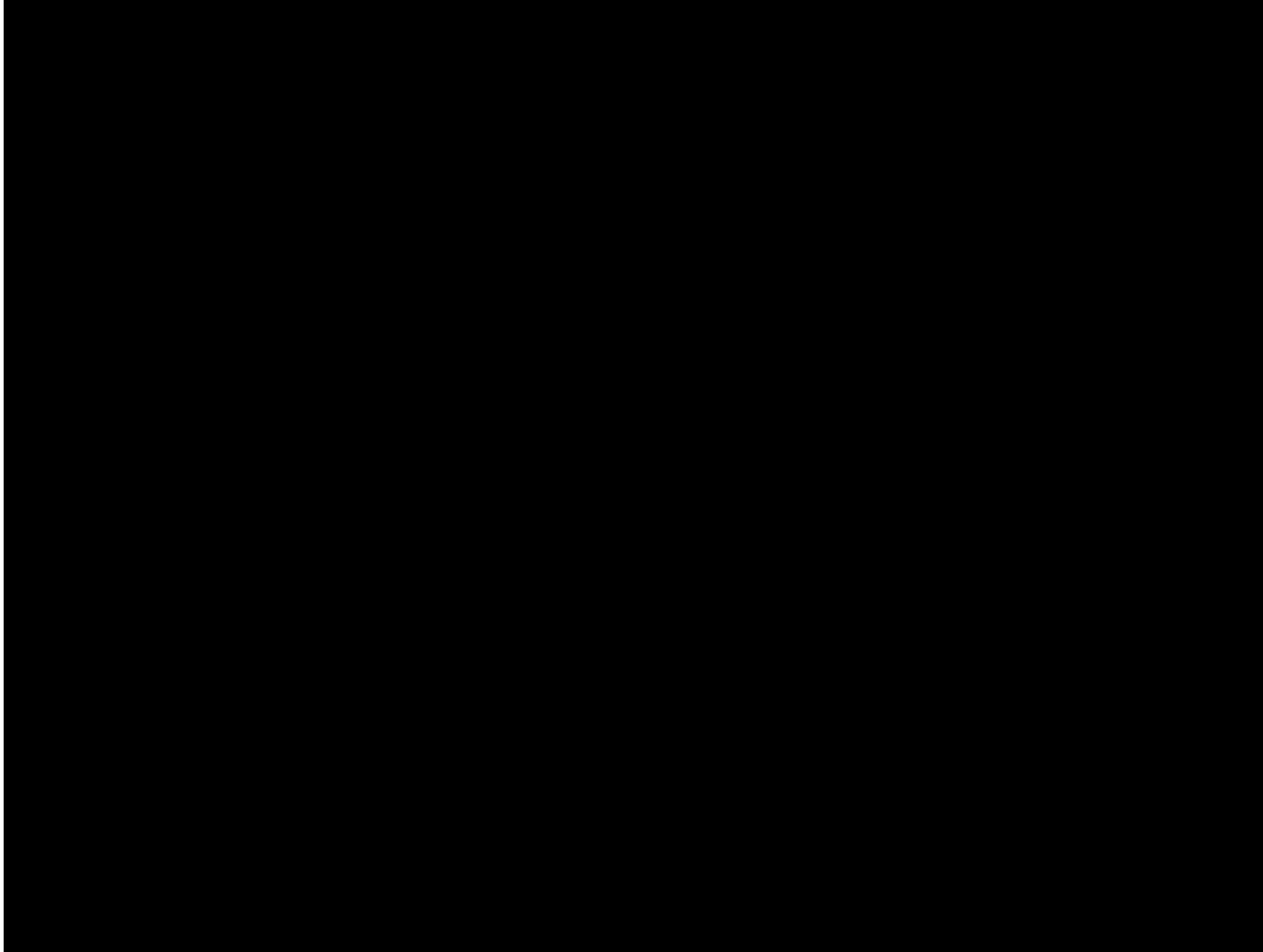
- **Explore high T and/or high P phases**

  - **Experiments difficult to do**

- **Materials under planetary core conditions**

  - **E.g. phase diagram of high P hydrogen**

    - Sequence of candidate phases / structures

    - Characterize optical properties using GW

    - 2-phase coexistence MD for melting

  - **E.g. shock compression of quartz**

    - Non-equilibrium properties and phases …

- 4725 atoms (672 in flyer plate) for 2 ps
- Shock = 6 km/s ~ speed of sound in quartz
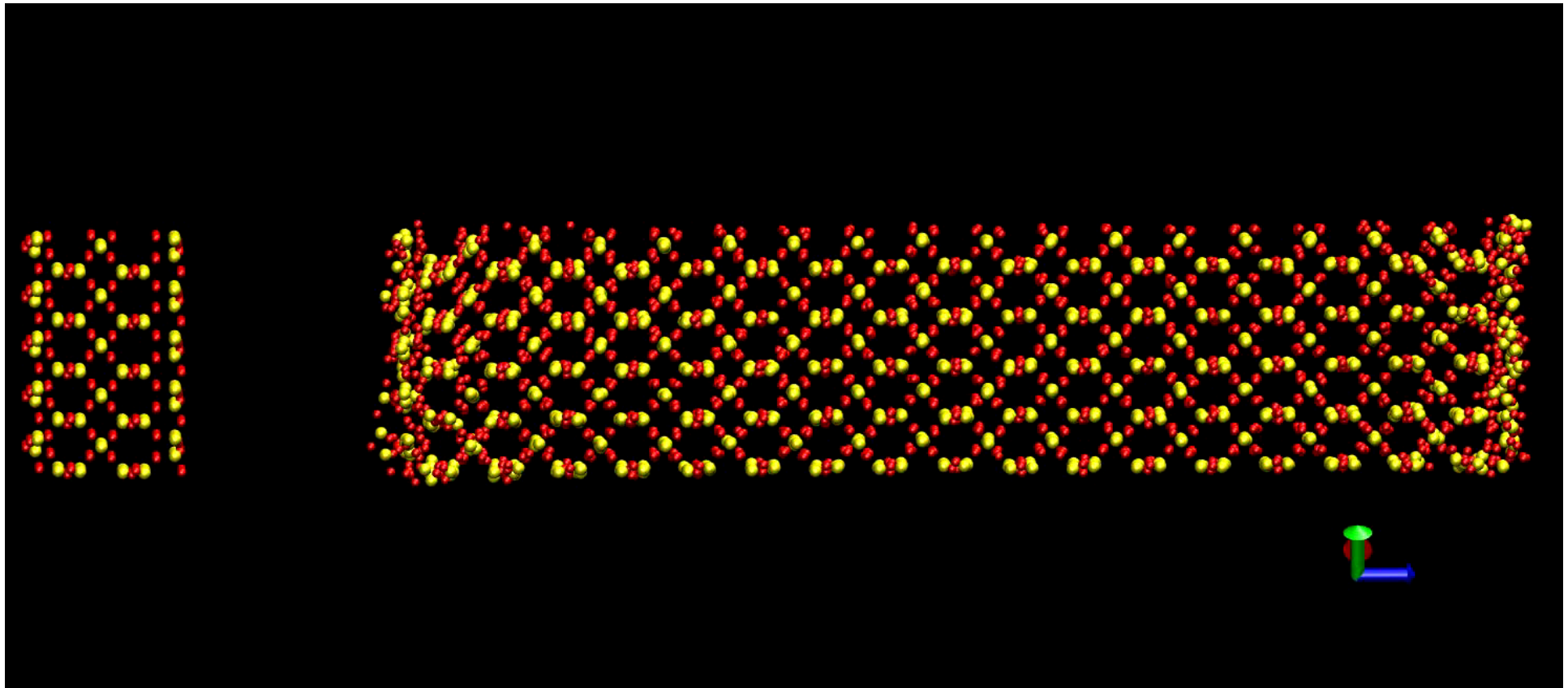
Dynamically Stabilized Growth of Polar Oxides: The Case of MgO(111)

Phys. Rev. Lett. **107**, 056101 (2011)

Vlado K. Lazarov, Zhuhua Cai, Kenta Yoshida, K. Honglian,

L. Zhang, M. Weinert, Katherine S. Ziemer and Philip J. Hasnip

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- ### MgO is an important polar oxide

  - #### Key substrate for growth

- ### MgO(001) films are nice and well-ordered

- ### MgO(111) films are usually poor with

  - #### Interface roughness

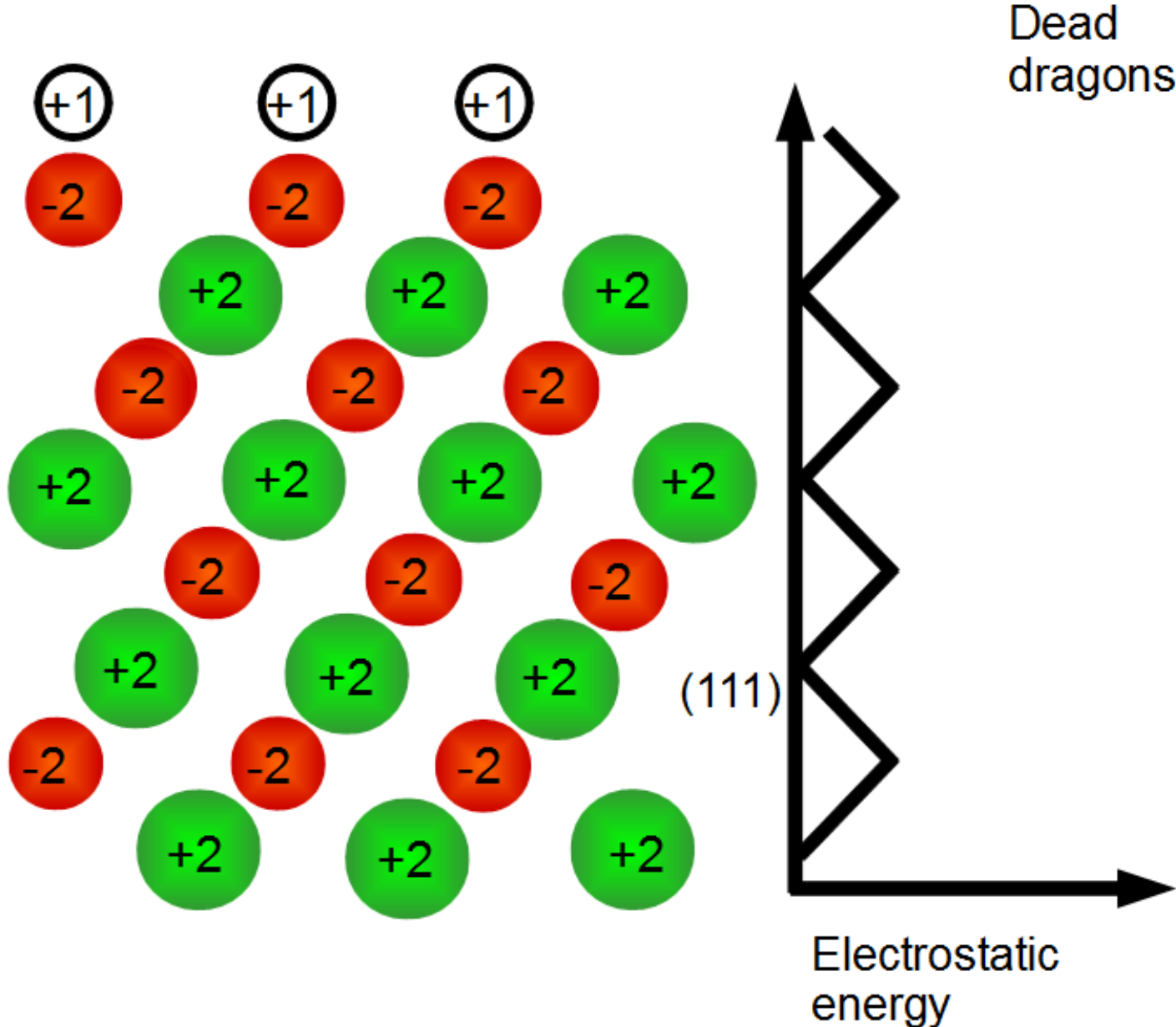 - #### Surface faceting

  - #### Surface reconstructions

  - #### Atomic mixing

  - #### Why?
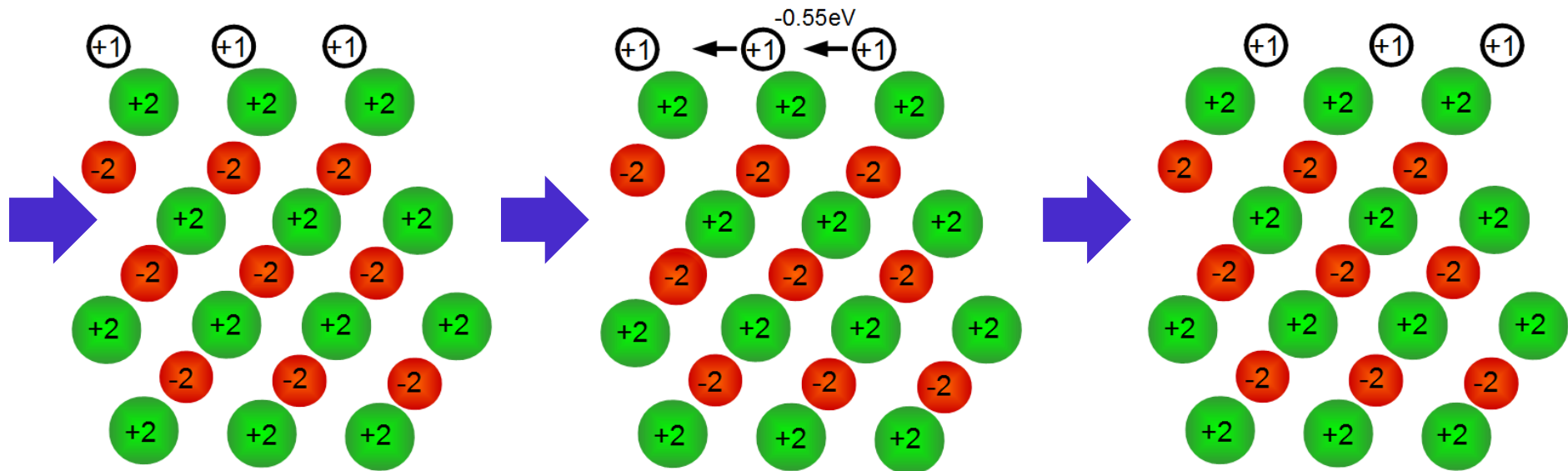
Simple electrostatic model
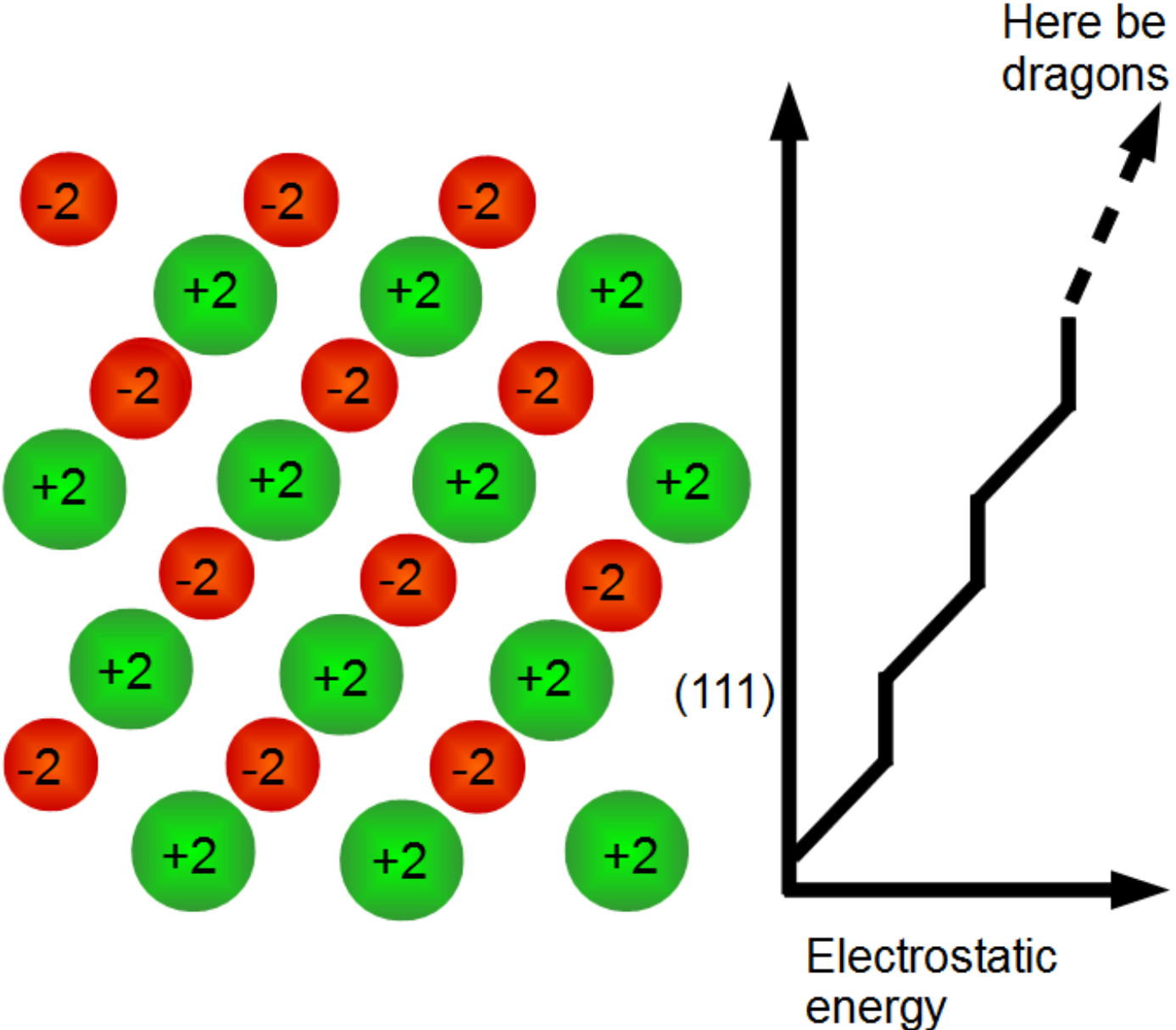
Hydrogen to the rescue

What about growth?
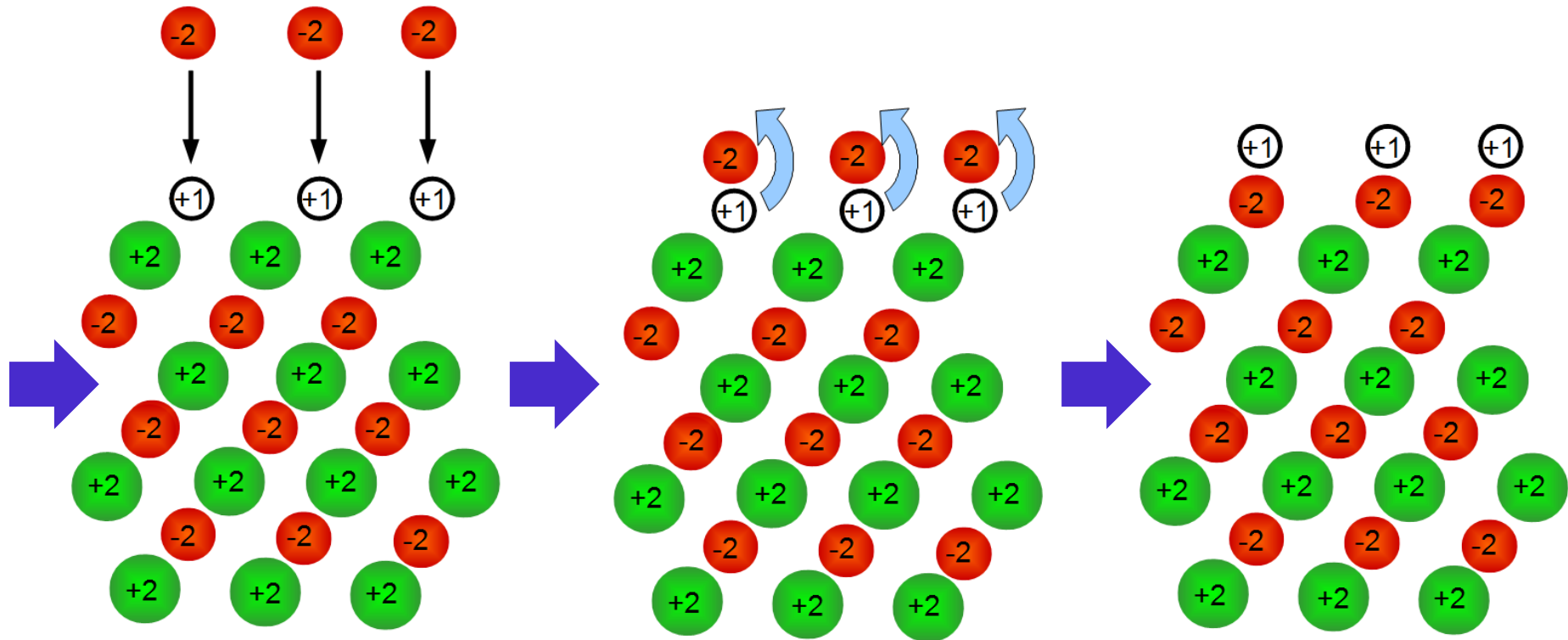
- If hydrogen can stabilize the surface by passivation can it help with growth? Can we simulate using CASTEP?

- First phase – add Mg and relax …

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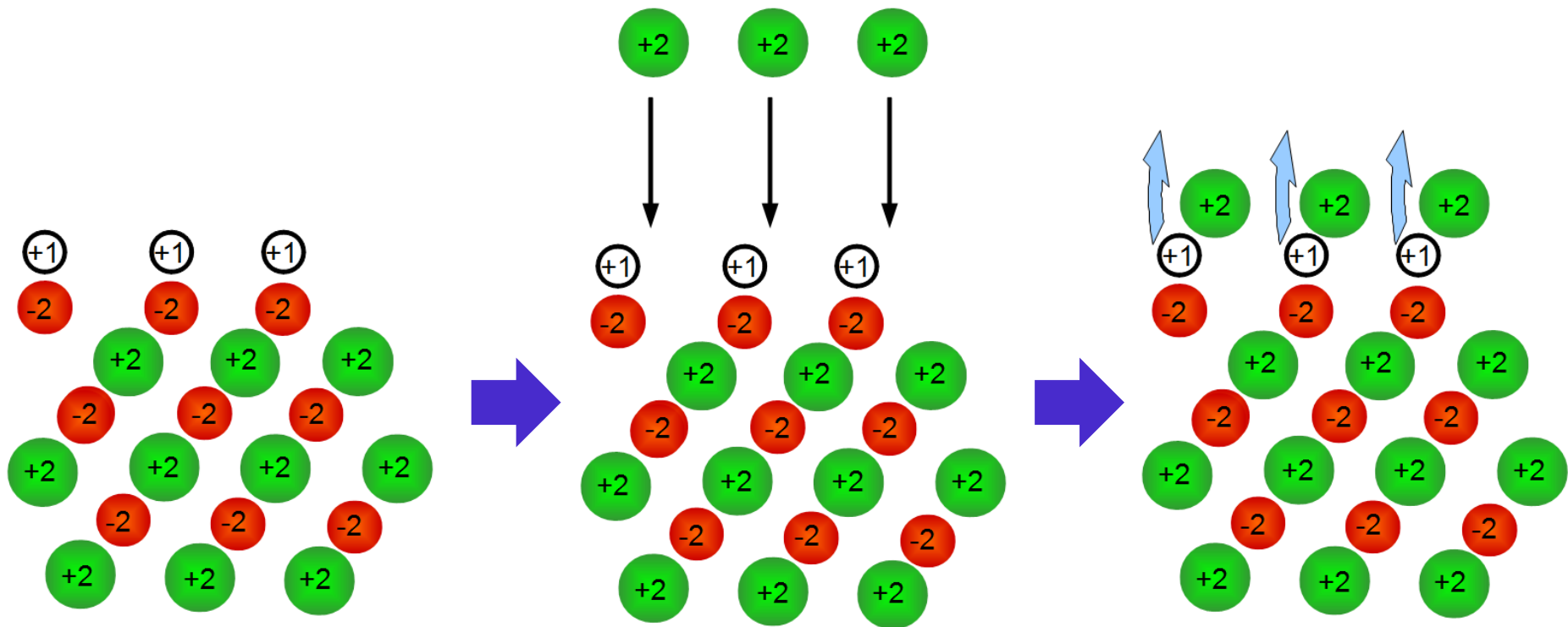
- Second phase – hydrogen spontaneous relaxation:

- Third phase – add O and relax …

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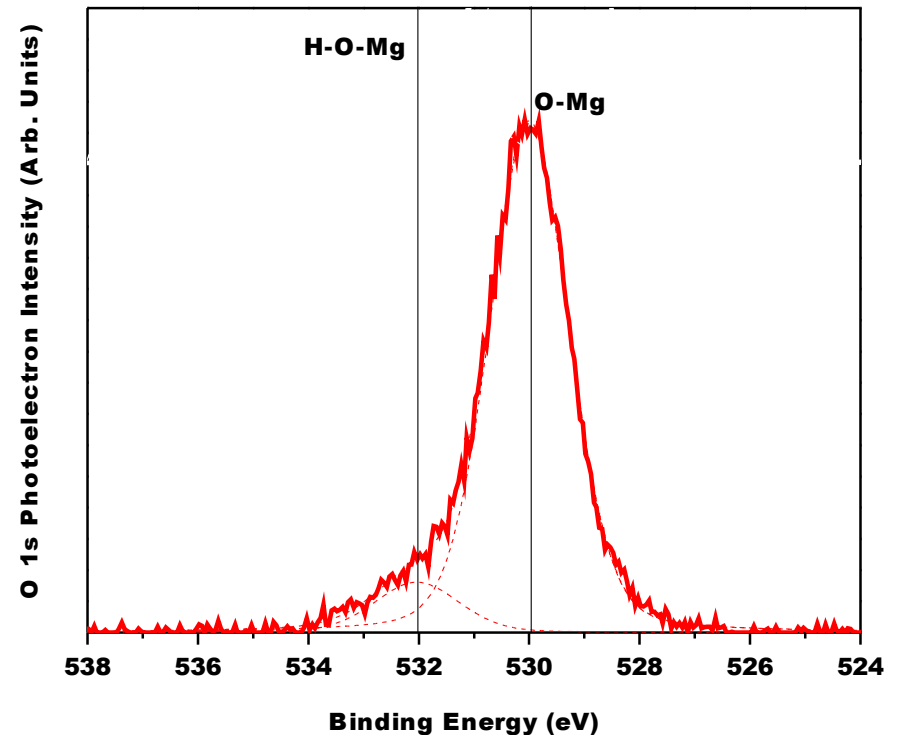
- A mechanism for growing high quality MgO(111) films
  - Hydrogen acts to heal surface dipole dynamically
  - Acts as a surfactant and is not trapped within MgO

TEM of MgO(111) on SiC substrate

Photoelectron spectroscopy

Summary

- ## QM of materials is hard

  - ### Many interacting particles

- ## DFT makes QM of materials feasible

  - ### One key unknown – the exact V_{xc}

- ## CASTEP is a robust and reliable implementation of DFT for periodic systems

  - ### Wide feature set

  - ### User friendly for theory and experimentalists

  - ### Fast and scalable

- Hohenberg & Kohn, Phys. Rev. B **136**, 864 (1964)

- Kohn & Sham, Phys. Rev. A **140**, 1133 (1965)

- MC Payne et al., Rev. Mod. Phys **64**, 1045 (1992)

- RM Martin, *"Electronic Structure: basic theory and practical methods"*, Cambridge University Press (2004)

- SJ Clark, MD Segall, CJ Pickard, PJ Hasnip, MIJ Probert, K Refson and MC Payne, *"First principles methods using CASTEP"*, Zeitschrift für Kristallographie **220**, 567 (2005)

- V Milman, K Refson, SJ Clark, CJ Pickard, JR Yates, S-P Gao, PJ Hasnip, MIJ Probert, A Perlov and MD Segall, *"Electron and vibrational spectroscopies using DFT, plane waves and pseudopotentials: CASTEP implementation"*, J. Molec. Structure: THEOCHEM (2010)