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Introduction to electronic structure, plane waves and pseudopotentials

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Overview of lecture

- What is electronic structure?
  - Density Functional Theory
  - Periodicity and Bloch’s Theorem
  - Bloch’s Theorem and k-points
- Plane wave basis set
- Pseudopotentials

- NB Colour slides are available on the website

Electronic Structure

What is Electronic Structure?

- The properties of materials and chemicals are governed by their electrons.
  - It is the electrons which determine whether atoms are bonded or not
  - And what type of bonds are formed (e.g. ionic, covalent, metallic, Van der Waals).
- The term ‘electronic structure’ is used to describe how the electrons are spread around a crystal or molecule.

First Principles Modelling

- A.k.a. *Ab Initio* = “From the beginning”
  - Using laws of Quantum Mechanics
  - No fitting to experimental data
- In quantum chemistry, usually taken to mean Hartree-Fock theory

  (or beyond e.g. MP2, CI, etc)
- In physics, usually taken to mean DFT

  (or beyond e.g. GW, QMC, etc)

Advantages of *Ab Initio*

- High accuracy and predictive ability
  - not limited by the fitting data-set
  - can cope with unusual environments, and bond breaking/making
  - wide range of properties can be calculated
- BUT computationally expensive
  - limited in size of system can study
  - need powerful computers

Which *Ab Initio*?

- In this module, will focus on DFT
    - Density Functional Theory
        - widely used in academia + industry
        - good balance of accuracy and speed
    - There are some limitations
        - One uncontrolled approximation at its heart
        - More advanced forms of QM can avoid this but MUCH more expensive and limited to study of small systems

What is DFT?

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?

Simple Quantum Mechanics

- 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?

Real materials

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

$$\left\{-\frac{\hbar^2}{2}\left(\frac{\nabla^2_{n1}}{m_1}+\ldots+\frac{\nabla^2_{nM}}{m_M},\frac{\nabla^2_{e1}}{m}+\ldots+\frac{\nabla^2_{eN}}{m}\right)\right.$$
$$\left.+\hat{V}\left(\mathbf{R}_1,\ldots,\mathbf{R}_M,\mathbf{r}_1,\ldots,\mathbf{r}_N,t\right)\right\}\Psi\left(\mathbf{R}_1,\ldots,\mathbf{R}_M,\mathbf{r}_1,\ldots,\mathbf{r}_N,t\right)$$
$$=i\hbar\frac{\partial\Psi\left(\mathbf{R}_1,\ldots,\mathbf{R}_M,\mathbf{r}_1,\ldots,\mathbf{r}_N,t\right)}{\partial t}$$

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

Born-Oppenheimer approximation

- Compared to electrons, nuclei are heavy and slow ($m_e << m_p$)
  - Electrons react "instantly" to nuclear motion
  - Nuclear wavefunction very localized
    - Can break down for light atoms and/or low T
  - Concentrate QM effort on electrons
  - No need for time dependent QM
  - This is the Born-Oppenheimer approximation:

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

Enter DFT

- 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

DFT Fundamentals

- H-K Theorem
  - The groundstate energy *E* ONLY depends on the electron density $\rho\left(\mathbf{r}\right)$
  - And the mapping is unique via a **universal** functional $E = E\,[\rho]$
- K-S Equations
  - The groundstate energy *E* and density $\rho\left(\mathbf{r}\right)$ of electrons are exactly the same as those of *non-interacting* particles, iff we include an extra potential – the *exchange-correlation potential* = V_{xc}

Kohn-Sham Problems

- Do not know how to calculate the Kinetic Energy of a density!
  - But we can do this for a wavefunction
  - Introduce fictitious *single-particle* orbitals that give the correct density and for which *can* calculate KE
- Do not know the universal functional
  - Write in terms of things we do know, e.g. electron-electron interaction so the unknown bits are “small” and hence can be easily approximated as a single “exchange-correlation” (XC) functional.

Kohn-Sham Equations

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

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

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

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

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

Exchange-Correlation Functional

- DFT is formally exact but in practice we need to approximate E_{xc}
  - The LDA assumes that $E_{xc}[\rho](\mathbf{r})$ at some point **r** is the same as if *every* point had same density
  - Hence LDA is fitted to Homogenous Electron Gas data calculated with high level QM methods
    - expected to be good for metals
    - actually works well for many systems!
    - tends to overbind energies and shorten bonds
  - More advanced approximations are available – see later lectures …

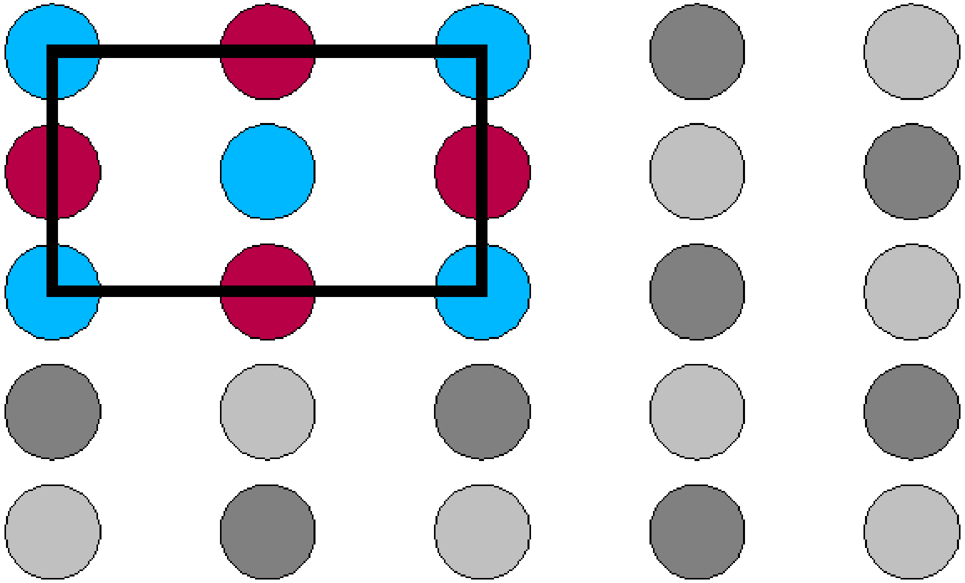
Why Bother?

- Many-body QM is hard
  - It is impossible to solve the Schrödinger equation exactly for all but the most simple problems
  - Numerical approaches expand unknown wavefunction in terms of known basis functions and unknown coefficients
  - a simple spin system with 20 particles needs 2^{20} coefficients (spin up & down)
  - exponential scaling is bad!
- DFT is easy
  - uses a 3D scalar field instead – much better!

Periodicity and Bloch's Theorem

Physics to the rescue …

- But we still have *N*~10^{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* …



Bloch's Theorem

- A fundamental theorem of condensed matter physics
- If the nuclei are arranged periodically then the potential and density must be periodic:

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

- *Bloch's Theorem*: Hence the wavefunction must be 'quasi-periodic':

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

- 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.

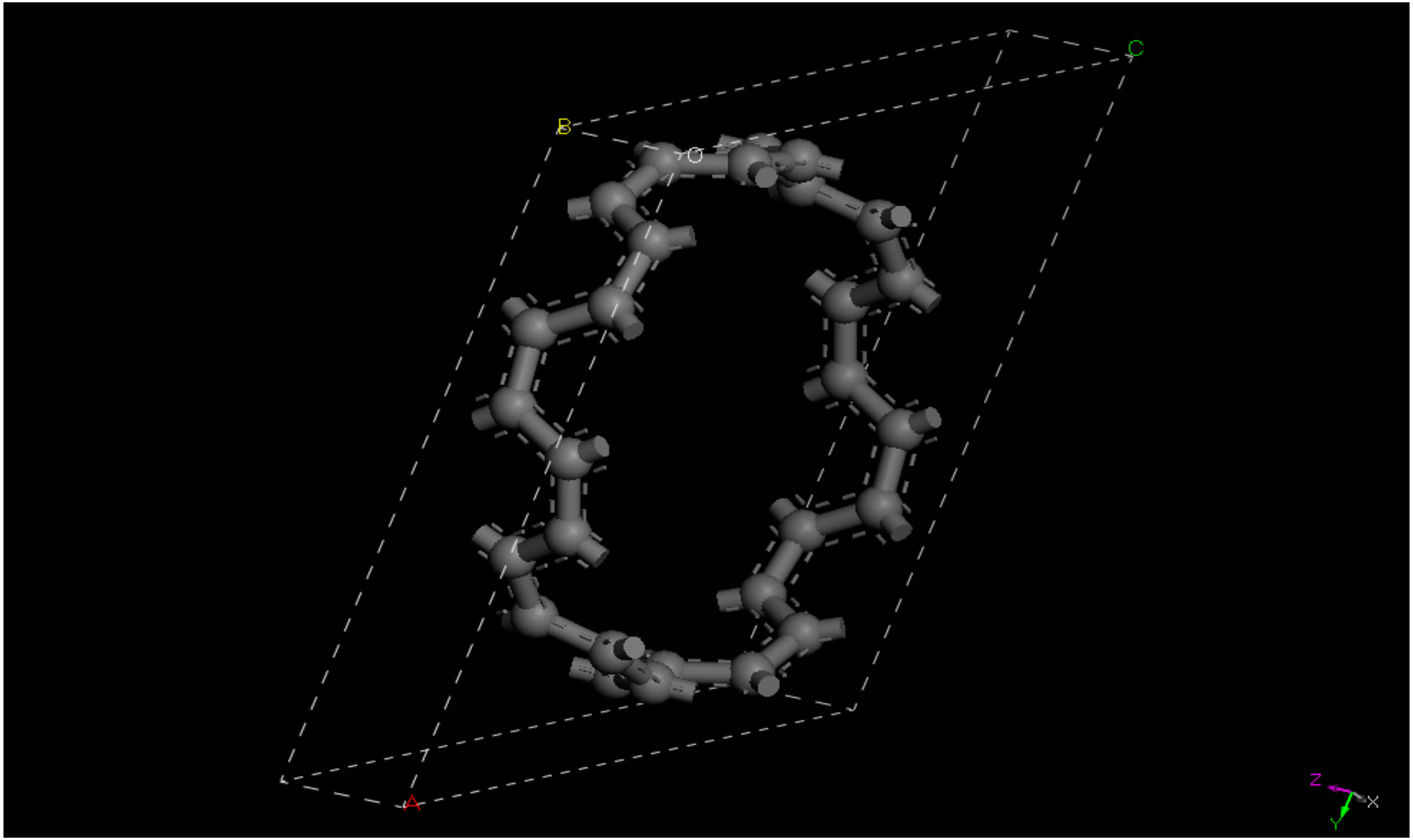
Exploiting Periodicity

- So now we only have to solve the K-S equations in a single unit cell
  - Hence N~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.

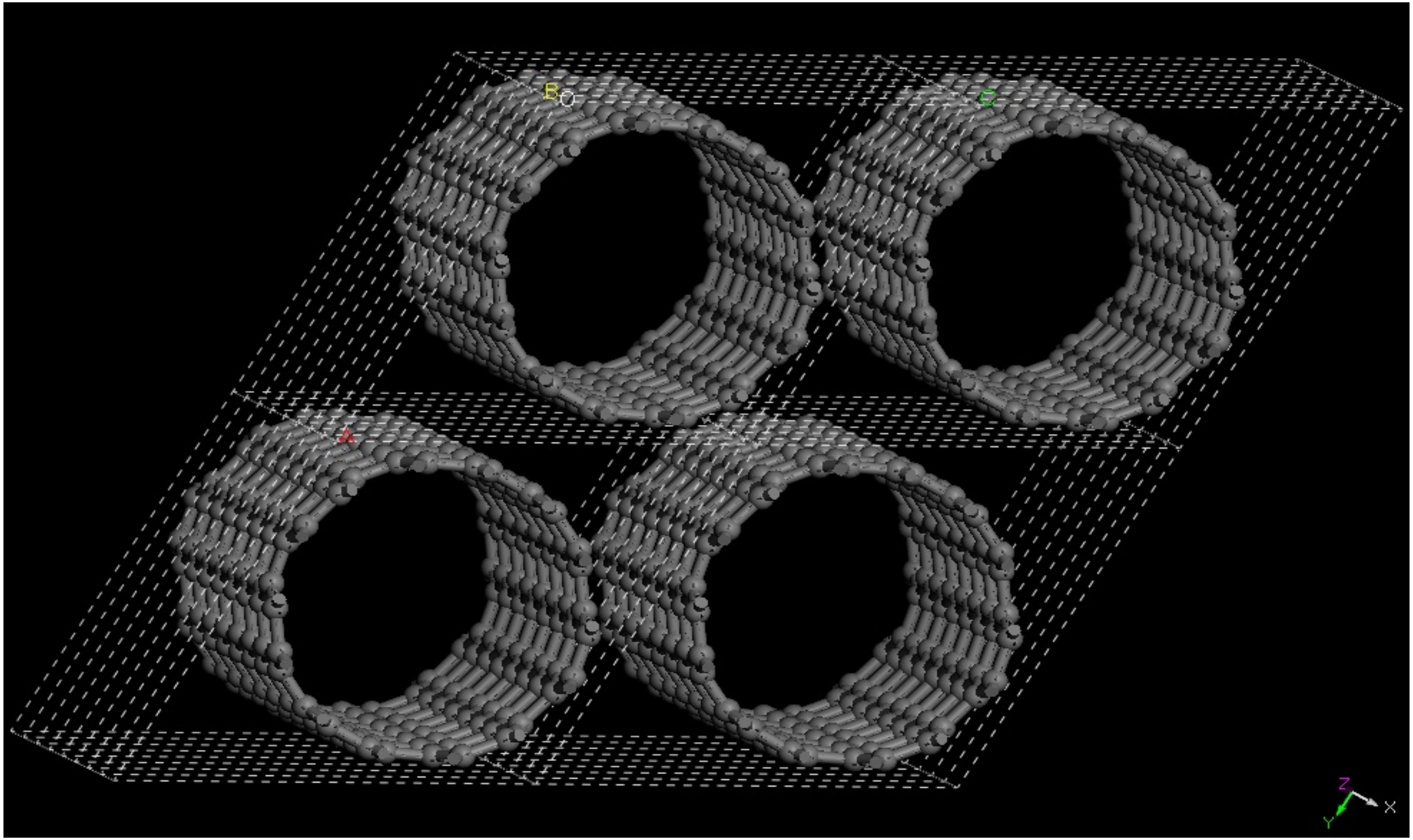
Supercell Approximation

- What if want to calculate properties of a crystal defect? or an isolated molecule? or a surface?
- Use a *supercell*
  - e.g. put 1 defect into a 2x2x2 cell
  - e.g. add vacuum around molecule
  - e.g. add vacuum above surface

Nanotube Primitive Cell



Nanotube Supercell



K-points

More Bloch's Theorem

- Bloch's Theorem says that in a periodic potential wavefunction is quasi-periodic

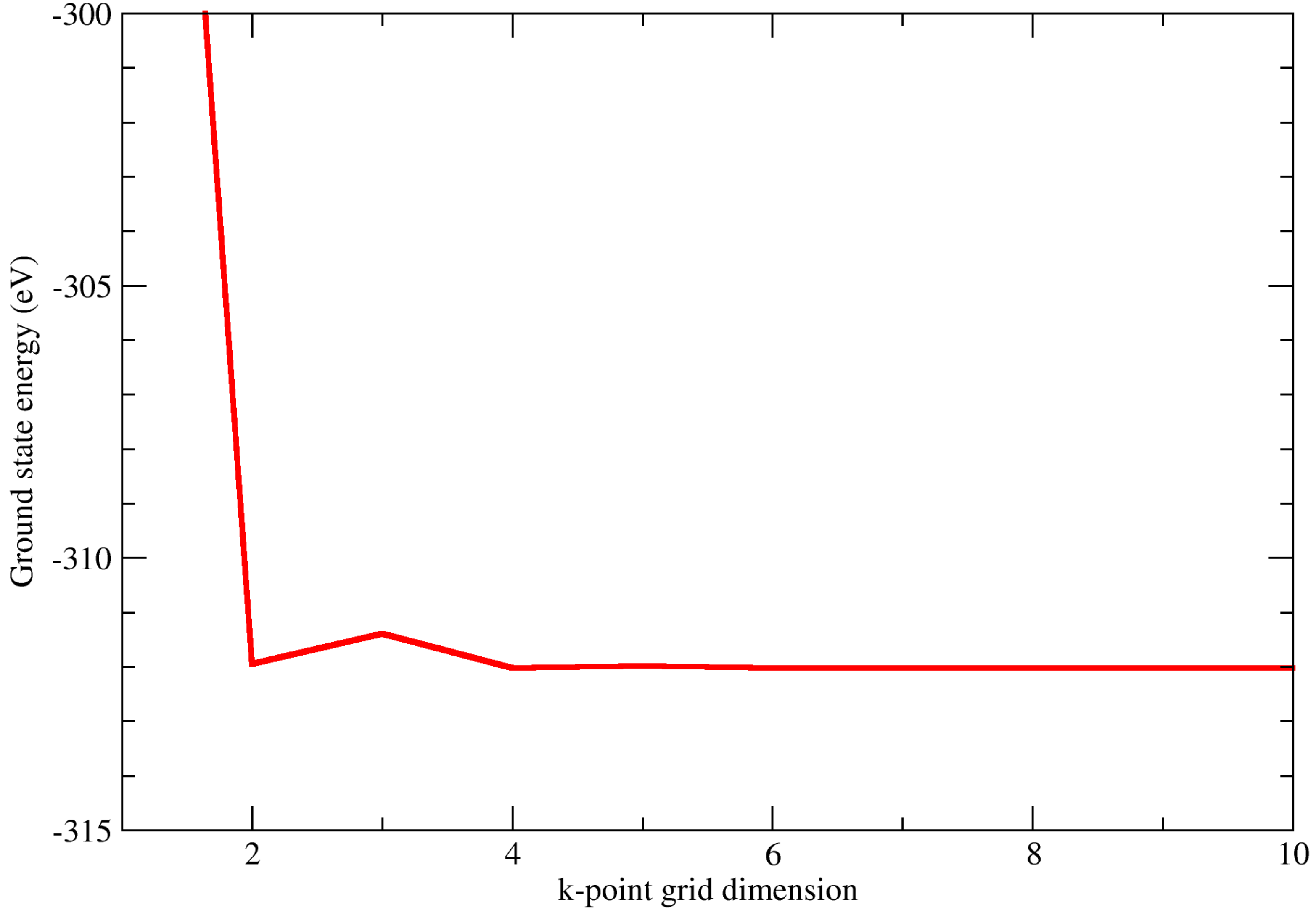
$$\psi_k(\mathbf{r}) \quad = \quad e^{i\mathbf{k}.\mathbf{r}} u_k(\mathbf{r})$$

- Neighbouring cells vary by phase factor
- Hence need to integrate over all possible values of **k** when constructing density:

$$\begin{aligned}\rho(\mathbf{r}) &= \int |\psi_k(\mathbf{r})|^2 d^3\mathbf{k} \\ &\approx \sum_k |\psi_k(\mathbf{r})|^2\end{aligned}$$

K-point sampling

- Convergence required for periodic calculation:



BZ sampling

- We sample the k-points within the 1st Brillouin zone (dual of real-space unit cell)
- Number of points depends on size of BZ
    - As zone gets smaller (larger real-space cell) then need less k-points
    - Standard sampling is a Monkhorst-Pack mesh
    - Need dense sampling for metals to capture discontinuity in band occupancy at $E=E_F$
    - Can use crystal symmetry to reduce number

Planewaves

Kohn-Sham Equations

- Rewrite the many-body Schrödinger equation for *N* electrons into *N* 1-particle equations:

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

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

- And occupy each band *b* with 2 electrons
- This looks like a set of eigenvalue equations …

Periodicity and Basis Sets

- How can we represent a wavefunction or density in a computer?
  - Real-space grid will require very dense mesh to get required resolution
  - Alternatively could write it in terms of coefficients of known basis functions …
- Obvious basis set for periodic system is 3D sine and cosine functions -> Fourier series and so can combine with Bloch's theorem:

Plane waves and Fourier Series

- 3D Fourier basis (also known as *plane waves*):

$$\psi_k(\mathbf{r}) \;=\; \sum_G c_{Gk} e^{i(\mathbf{G}+\mathbf{k}).\mathbf{r}}$$

- where c_{Gk} are unknown complex coefficients
- The sum is over all wavevectors **G** which fit the unit cell and **k** comes from Bloch's theorem
- Hence ψ_k is a vector of coefficients c_{Gk}

Which plane waves are allowed?

- Not all values of **G** are allowed
  - Have to be reciprocal lattice vectors
  - Smallest **G** is given by largest wavelength in real space: $G_{min}=2\pi/a$
  - Hence form a discrete set
- If we make the unit cell longer in one direction then the allowed wavevectors in that direction become shorter
- But still an infinite set?

Cut-off energy

- In practice the coefficients c_{Gk} associated with larger **G** become smaller and smaller
  - Corresponds to finer real-space resolution in description of density etc.

$$|\mathbf{G}| \to \infty,\ |c_{Gk}| \to 0$$

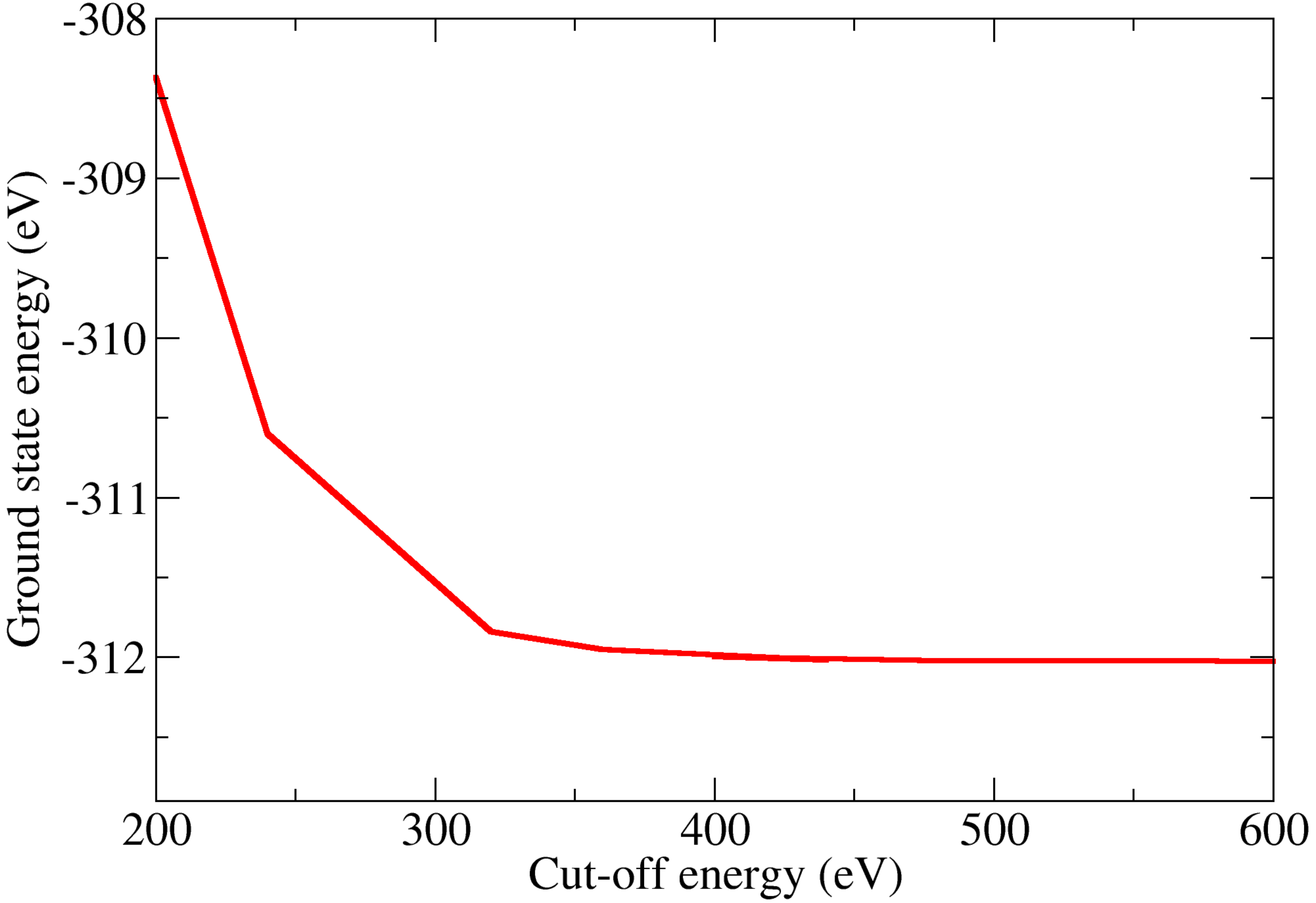
- Hence can truncate set at a largest $\mathbf{G}_{\mathrm{max}}$
- Express as the cut-off energy:

$$E_{cut} = \frac{\hbar^2}{2m} \left|\mathbf{G}_{max}\right|^2$$

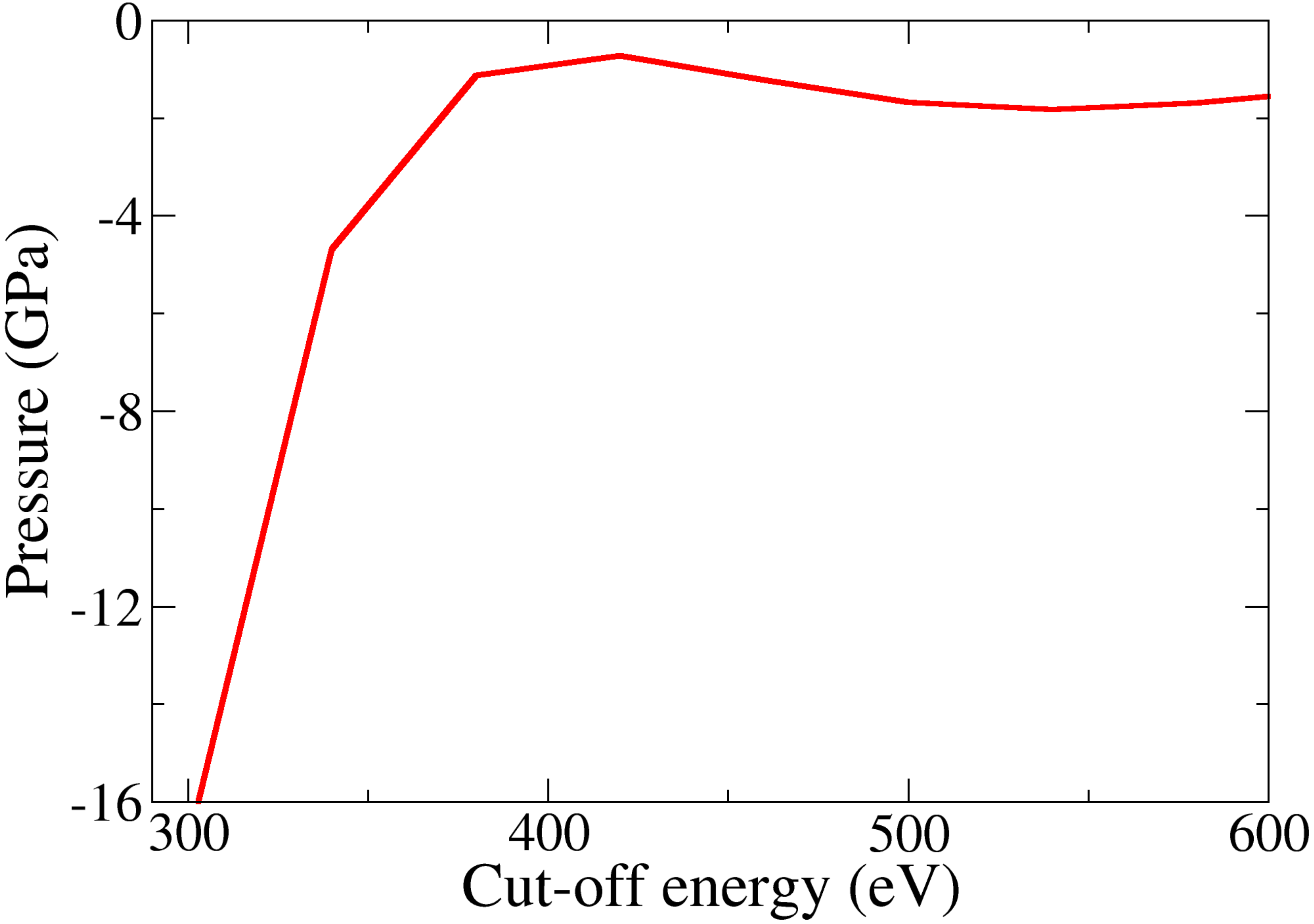
Convergence

- The cut-off energy is a key convergence parameter
  - Larger values always correspond to better results but need more computer time & memory
  - The ground state energy obeys variational principle and hence increasing E_{cut} adds more variational freedom and hence montonically improves the quality of the density and lowers the ground state energy
  - Not all properties are variational …

Convergence of E_0



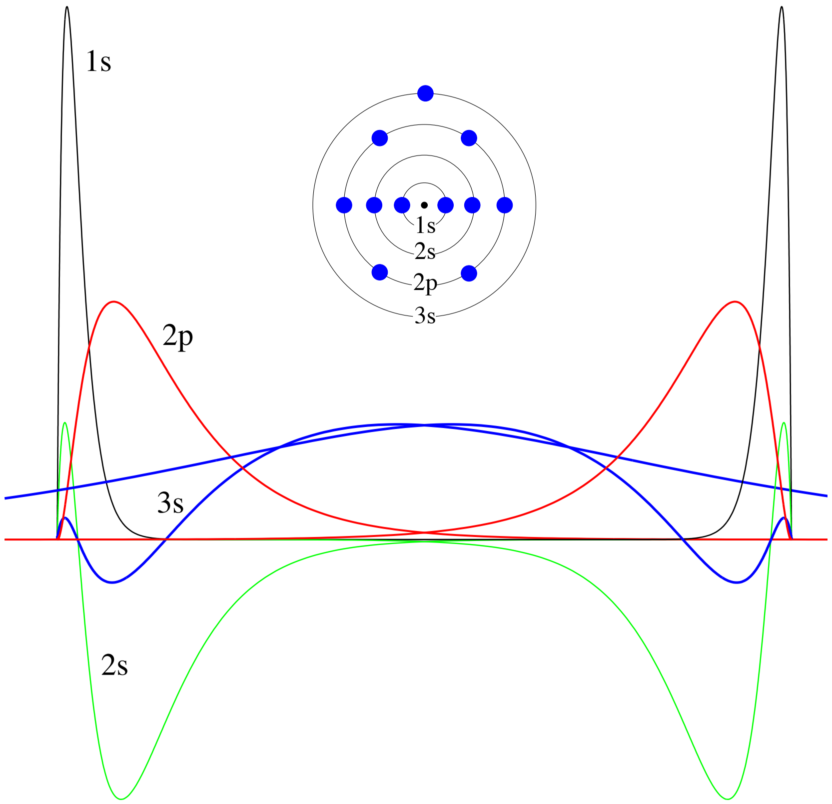
Convergence of pressure



Pseudopotentials

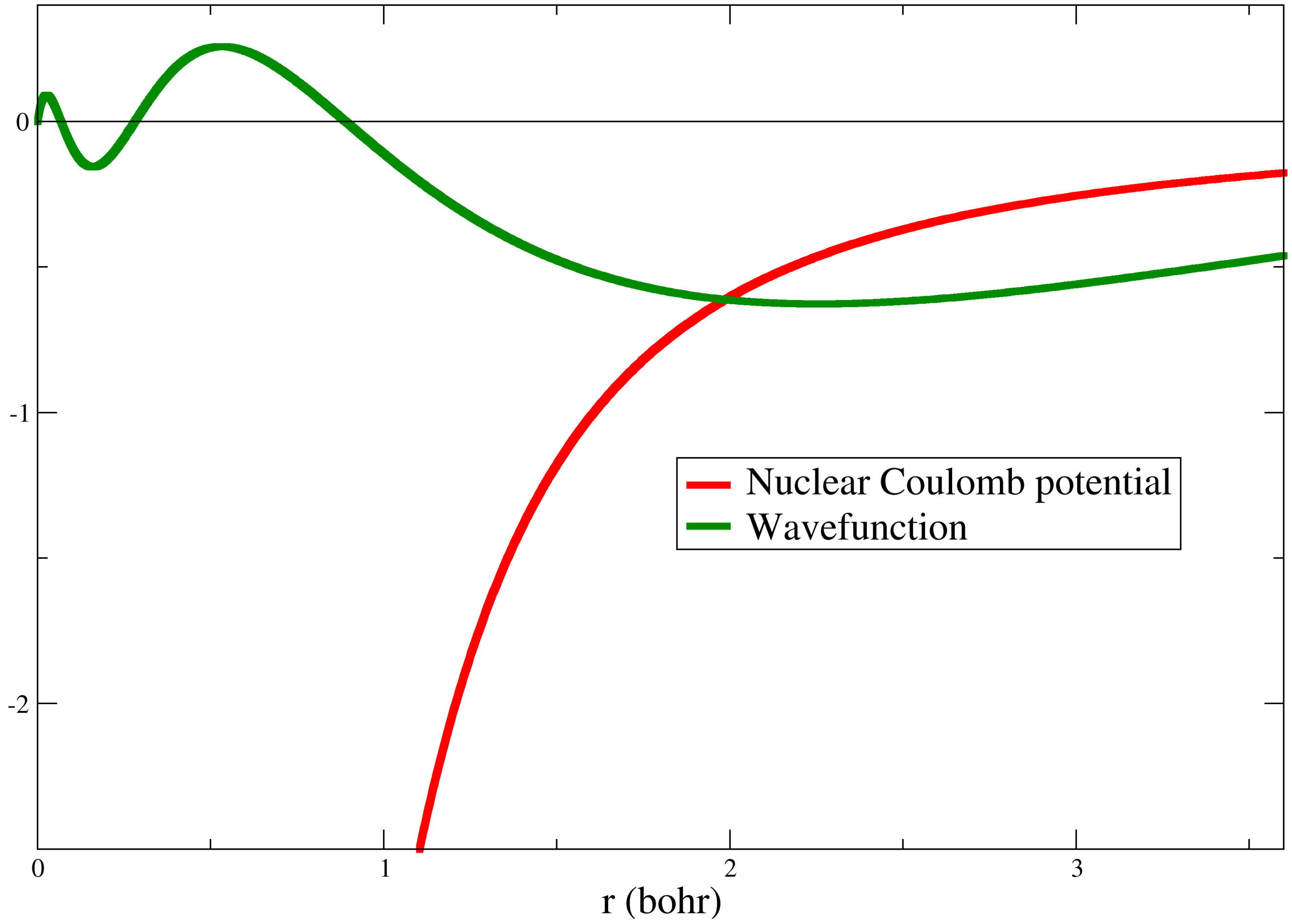
Why do we need them?

- Chemical bonding arises from overlap of outer electrons
- Core states approximately inert and insensitive to environment
- Hence combine inner electrons with nucleus to make a pseudo-ion



More

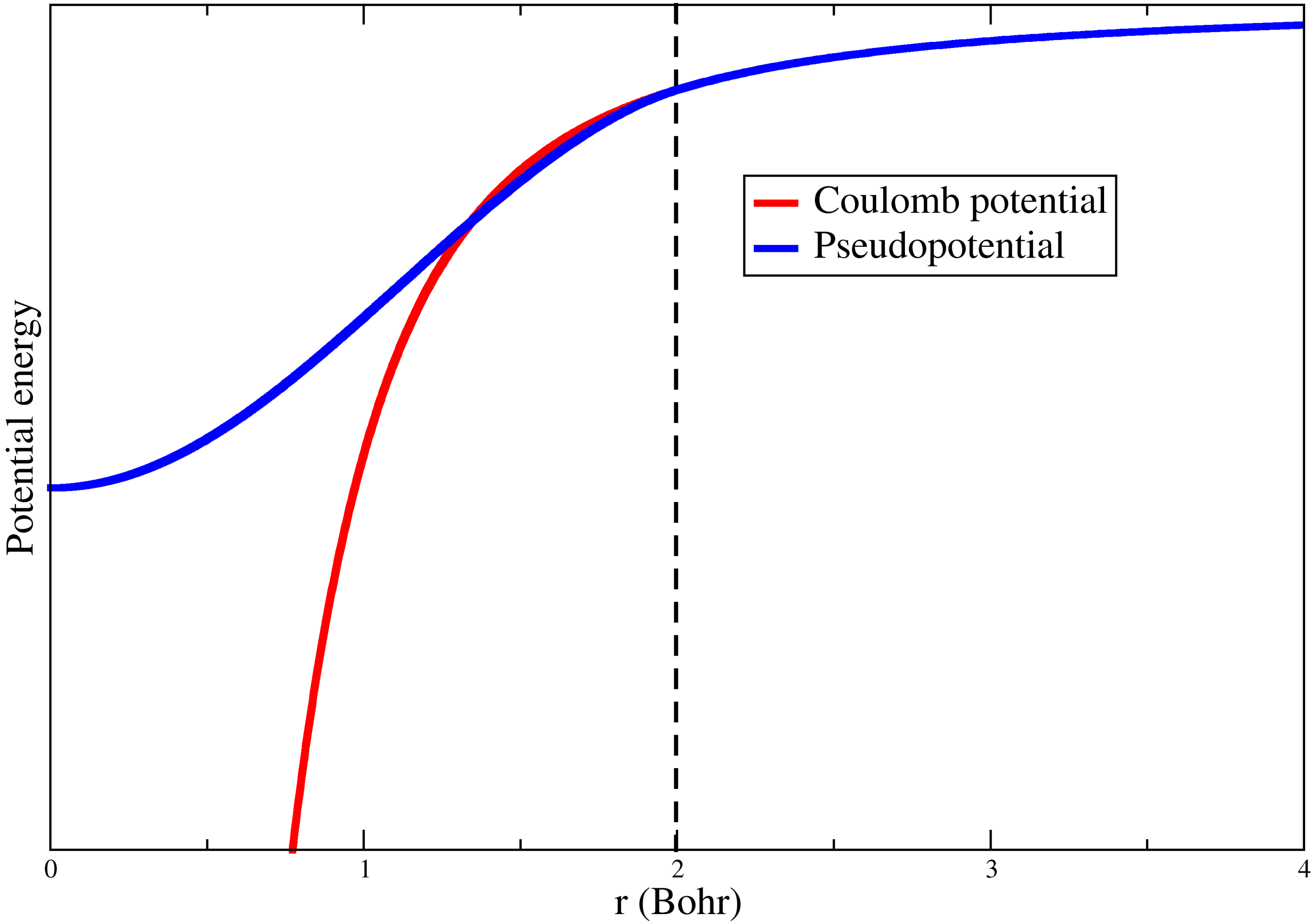
- But as well as reducing the number of electrons, there is another advantage:



Wavefunction near nucleus oscillates – required for orthogonality with inner states

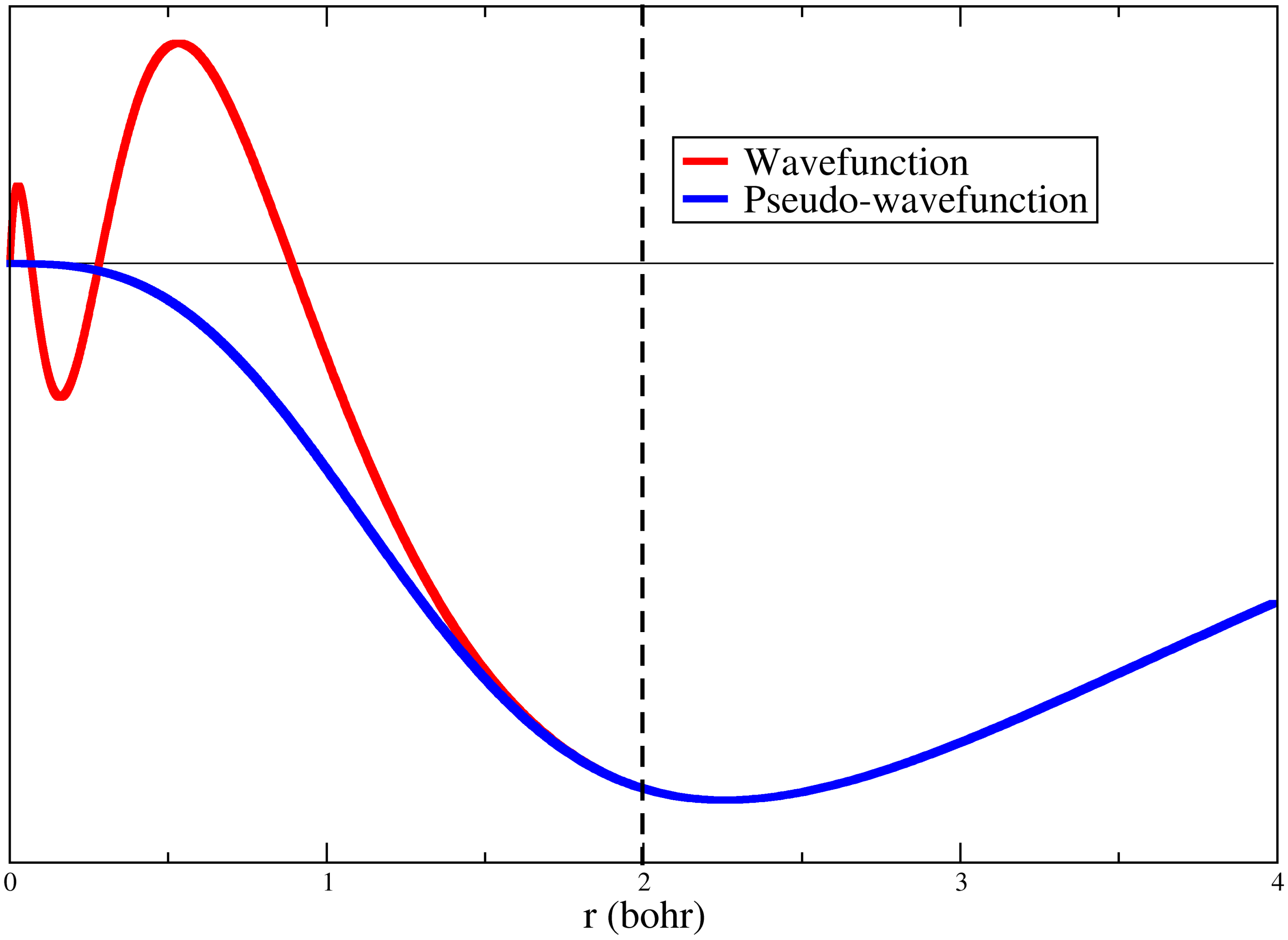
More

- So we can replace the Coulomb potential of nucleus with a modified, weaker potential – the pseudopotential:



More

- And so pseudo-wavefunction is smoother and needs fewer plane waves to describe it!



Result?

- The core electrons are combined with nucleus to make an ion, saving electrons
- The outer electrons interact with this ion
- Pseudopotential constructed to have identical behaviour outside the ‘core radius’ (r_c) but fewer oscillations inside r_c where it does not affect any bonding etc
- Hence need fewer plane waves per state and fewer states!

Summary

Eigenvalue Equation

- DFT can be written in simple form using the K-S Hamiltonian operator:

$$\hat{H} \quad = \quad -\frac{\hbar^2}{2m}\nabla^2 + V\left[\rho\right](\mathbf{r})$$

- Hence the set of K-S equations can be rewritten as an eigenvalue problem:

$$\mathrm{H}[\rho]\psi_{bk} = \epsilon_{bk}\psi_{bk}$$

- Where the Hamiltonian $\mathrm{H}[\rho]$ is an Hermitian matrix of size $N_G x N_G$ and ψ_{bk} is a vector of N_G Fourier coefficients for each k-point

Summary

- Bloch’s Theorem and periodicity greatly simplify the problem
  - Need to use k-points to sample BZ
  - Use supercells for non-periodic systems
- Plane waves are a natural basis set
  - Single parameter E_{cut} to determine quality
- Pseudopotentials remove unimportant electrons from the problem
  - And reduce the E_{cut} needed

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Useful References

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