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 will be available on VLE
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
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?
The 1-particle Schrödinger equation is:

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

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:

$$\left\{ -\frac{\hbar^2}{2} \left( \frac{\nabla^2}{m_1} + \ldots + \frac{\nabla^2}{m_M}, \frac{\nabla^2}{m}, + \ldots + \frac{\nabla^2}{m} \right) \right\} \psi (R_1, \ldots, R_M, r_1, \ldots, r_N, t)$$

$$+ \hat{V} (R_1, \ldots, R_M, r_1, \ldots, r_N, t) \right\} \psi (R_1, \ldots, R_M, r_1, \ldots, r_N, t)$$

$$= i\hbar \frac{\partial \psi (R_1, \ldots, R_M, r_1, \ldots, r_N, t)}{\partial t}$$

For a few grams of material we typically have $M \approx 10^{23}$ and $N \approx 10^{24}$. 
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:
  \[
  \psi \left( R_1, \ldots, R_M, r_1, \ldots, r_N, t \right) \longrightarrow \psi \left( r_1, \ldots, r_N \right)
  \]
- 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 $\rho (r)$.
- And the mapping is unique via a universal functional $E = E [\rho (r)]$

K-S Equations

- The groundstate energy $E$ and density $\rho (r)$ of electrons are exactly the same as those of non-interacting particles, iff we include an extra potential – the exchange-correlation potential $= V_{xc}$
Do not know how to calculate the Kinetic Energy of a density!

- Can does 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 $\mathbf{r}$ is the same as if every point had the 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 $N \sim 10^{24}$ 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:
  \[ V(r + L) = V(r) \]
- **Bloch’s Theorem**: Hence the wavefunction must be ‘quasi-periodic’:
  \[ \psi_k(r) = e^{ik \cdot r} u_k(r) \]
- where \( u_k(r + L) = u_k(r) \) is periodic and \( e^{ik \cdot r} \) 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 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
  \[ \psi_k(r) = e^{i\mathbf{k} \cdot \mathbf{r}} u_k(r) \]
- Neighbouring cells vary by phase factor
- Hence need to integrate over all possible values of \( \mathbf{k} \) when constructing density:
  \[ \rho(r) = \int |\psi_k(r)|^2 d^3k \]
  \[ \approx \sum_k |\psi_k(r)|^2 \]
K-point sampling

- Convergence required for periodic calculation:

![Graph showing convergence of ground state energy with k-point grid dimension.](image-url)
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:

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

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

- And occupy each band \( b \) with 2 electrons

- This looks like a set of eigenvalue equations …
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:
3D Fourier basis (also known as plane waves):

\[ \psi_k(\mathbf{r}) = \sum_{\mathbf{G}} c_{Gk} e^{i(\mathbf{G}+\mathbf{k}).\mathbf{r}} \]

- where \( c_{Gk} \) are unknown complex coefficients
- The sum is over all wavevectors \( \mathbf{G} \) which fit the unit cell and \( \mathbf{k} \) comes from Bloch’s theorem
- Hence \( \psi_k \) is a vector of coefficients \( c_{Gk} \)
Which plane waves are allowed?

- Not all values of \( \mathbf{G} \) are allowed
  - Have to be reciprocal lattice vectors
  - Smallest \( \mathbf{G} \) is given by largest wavelength in real space: \( G_{\text{min}} = \frac{2\pi}{2a} \)
  - 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?
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.

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

- Hence can truncate set at a largest $G_{\text{max}}$

- Express as the cut-off energy:

$$E_{\text{cut}} = \frac{\hbar^2}{2m} |G_{\text{max}}|^2$$
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 $E_{\text{cut}}$ adds more variational freedom and hence monotonically improves the quality of the density and lowers the ground state energy
  - Not all properties are variational …
Convergence of $E_0$
Convergence of pressure

Cut-off energy (eV) vs Pressure (GPa)

- The graph shows the convergence of pressure with respect to cut-off energy.
- As the cut-off energy increases, the pressure initially increases sharply and then levels off.
- The cut-off energy range is from 300 to 600 eV.
- The pressure range is from -16 to 0 GPa.

Summary

- Convergence of pressure is a critical aspect in computational materials science.
- Techniques such as density functional theory (DFT) and Bloch's theorem are used to model these properties.
Pseudopotentials
Chemical bonding arises from overlap of outer electrons.

Core states are approximately inert and insensitive to environment.

Hence combine inner electrons with nucleus to make a pseudo-ion.
But as well as reducing the number of electrons, there is another advantage:

Wavefunction near nucleus oscillates – required for orthogonality with inner states
So we can replace the Coulomb potential of nucleus with a modified, weaker potential – the pseudopotential:
And so pseudo-wavefunction is smoother and needs fewer plane waves to describe it!
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
DFT can be written in simple form using the K-S Hamiltonian operator:

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

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

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

Where the Hamiltonian \( H[\rho] \) is an Hermitian matrix of size \( N_G \times N_G \) and \( \psi_{bk} \) is a vector of \( N_G \) Fourier coefficients for each k-point.
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 $E_{\text{cut}}$ to determine quality.

Pseudopotentials remove unimportant electrons from the problem.

- And reduce the $E_{\text{cut}}$ needed.
Useful References

- Kohn & Sham, Phys. Rev. A 140, 1133 (1965)
- MC Payne et al., Rev. Mod. Phys 64, 1045 (1992)