Electronic Structure Methodology 1

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Lecture Two

Working with Density Functional Theory

- In the last lecture we learnt how to write the total energy as a *functional* of the density $n(\mathbf{r})$:

$$E_{\mathrm{tot}} = \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r}) + T[n] + E_{\mathrm{H}}[n] + E_{\mathrm{xc}}[n]$$

- $T[n]$ was introduced as the kinetic energy of a system of non-interacting electrons with a density of $n(\mathbf{r})$
- But, just as for the $E_{\mathrm{xc}}[n]$ we don't know what this functional $T[n]$ is.
- As for $E_{\mathrm{xc}}[n]$, guesses can be made (e.g. Thomas-Fermi), but they are not good enough
- We must write $T[n]$ explicitly in terms of the independent electron *Kohn-Sham* orbitals.

The Kohn-Sham Equations

$$E_{\rm tot}[\{\psi_i\}] = -2\sum_i \frac{\hbar^2}{2m}\int \psi_i \nabla^2 \psi_i d\mathbf{r}$$
$$+ \int V_{\rm ion}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$
$$+ \frac{e^2}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$
$$+ E_{\rm xc}[n(\mathbf{r})] + E_{\rm ion}(\mathbf{R_i})$$

The charge density is written as:

$$n(\mathbf{r}) = 2\sum_i |\psi_i(\mathbf{r})|^2$$

The potentials are given by *functional* derivatives:

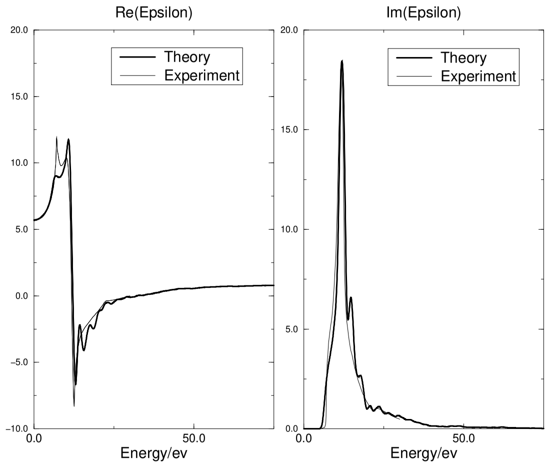
$V_{\rm xc}(\mathbf{r}) = \frac{\delta E_{\rm xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$ etc.

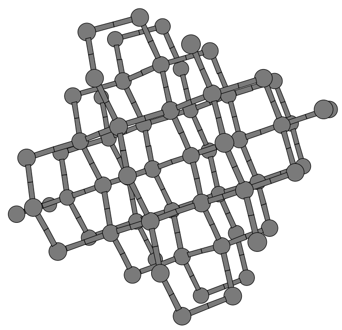
$$\boxed{[-\frac{\hbar^2}{2m}\nabla^2 + V_{\rm ion}(\mathbf{r}) + V_{\rm H}(\mathbf{r}) + V_{\rm xc}(\mathbf{r})]\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})}$$

The Kohn-Sham Orbitals

- The Kohn-Sham orbitals were introduced so that we can compute the independent electron kinetic energy corresponding to a charge density $n(\mathbf{r})$
- They need not have any physical meaning, nor need the Kohn-Sham eigenvalues
- However, experience shows that they do have some correspondence to the quasi-particle energy levels probed by spectroscopic techniques
- The so-called “band-gap problem”, to a good approximation, simply results in a rigid shift of the unoccupied energy levels

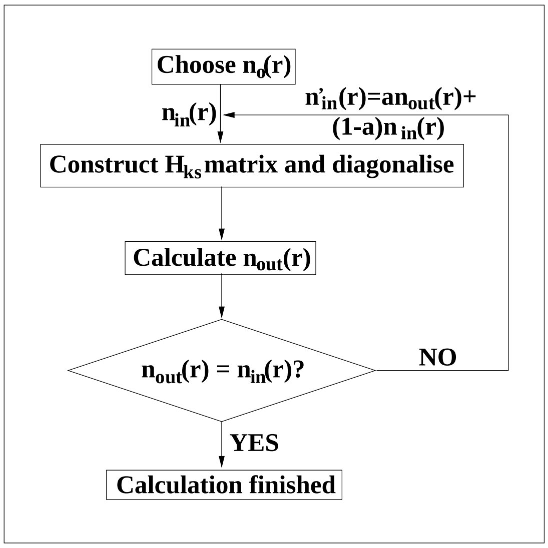
Dielectric Properties of Diamond





The complex dielectric function for diamond was calculated with a 0.7ev *Scissor* operator applied to the conduction bands

Being (self) consistent



- $V_H(\mathbf{r})$ and $V_{XC}(\mathbf{r})$ depend on $n(\mathbf{r})$
- $n(\mathbf{r})$ depends on $\{\psi_i(\mathbf{r})\}$
- But we are trying to find $\{\psi_i(\mathbf{r})\}$ and the corresponding energy levels — we need *self-consistency*

Solving an eigenproblem in a basis

- We have a problem of the form:

$$\hat{H}|\psi_i\rangle = \epsilon_i|\psi_i\rangle$$

- The wavefunctions are orthonormal:

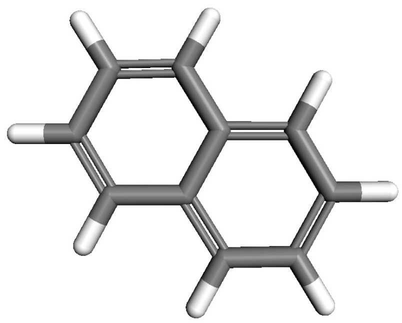
$$\langle\psi_i|\psi_j\rangle = \delta_{ij}$$

- If we choose a basis, we can construct a Hamiltonian as a matrix and diagonalise that matrix to get the eigenvectors and eigenvalues:

$$H_{ij} = \langle v_i|\hat{H}|v_j\rangle$$

$\boxed{\text{energy level} \longrightarrow \text{eigenvalue}}$ $\boxed{\text{wavefunction} \longrightarrow \text{eigenvector}}$

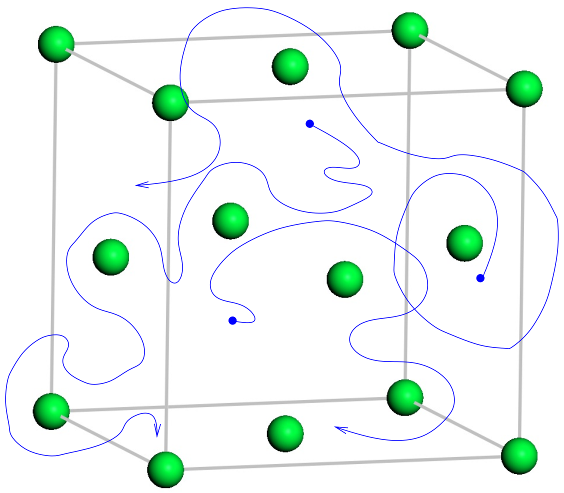
Just a few atoms



Naphalene

- Use a local basis set
  - possibly based on atomic orbitals
  - maybe some mathematically simple set like gaussians
- Build the Hamiltonian matrix
- Diagonalise
- This scales at $O(N^3)$

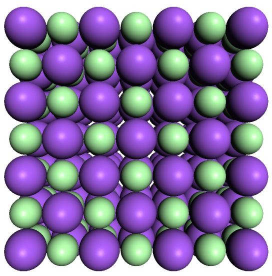
Electrons in Crystals



Cartoon of electrons (blue) in motion

- The electrons in a crystal experience a potential with the periodicity of the Bravais lattice: $U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r})$
- The scale of the periodicity is of the order of the de Broglie wavelength of an electron — 1Å— so we must use Quantum Mechanics
- Of course, the periodicity is an idealisation: impurities, defects, thermal vibrations, finite size effects

In a crystal



- Crystals contain $\approx 10^{23}$ atoms
- Direct diagonalisation of even a cluster of 10^3 atoms would be very costly

- So is it impossible?
- No!! Use symmetry . . .
  - crystals have translational symmetry (definition)
  - symmetry leads to a new quantum number, $\mathbf{k}$
  - use periodic boundary condition (PBCs) and you just have to worry about the atoms in the unit cell of the crystal

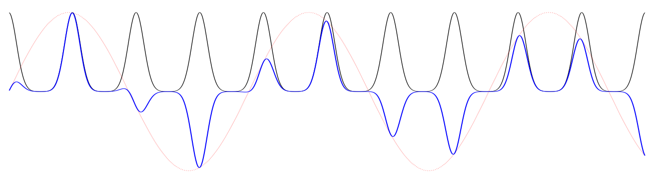
Periodic boundary conditions and Bloch's Theorem

$$\boxed{\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})}$$

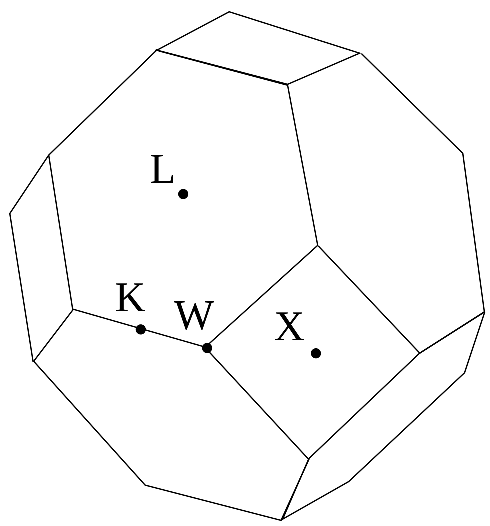
$$u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

$$\boxed{\Psi_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \Psi_{n\mathbf{k}}(\mathbf{r})}$$

- Independent electrons which obey the one electron Schrödinger equation for a periodic potential are called *Bloch electrons* and obey Bloch's theorem
- Bloch's theorem can be written in two equivalent forms



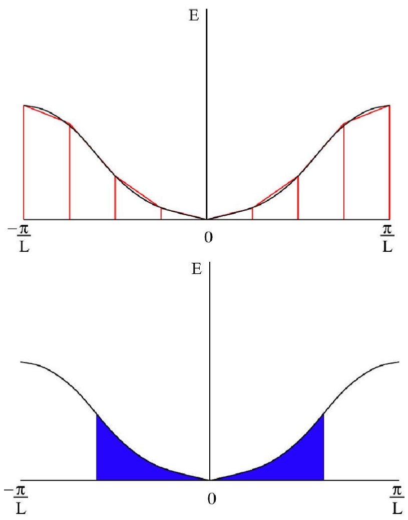
The First Brillouin Zone



The first FCC Brillouin zone

- The wave vector $\mathbf{k}$ can always be confined to the first Brillouin zone (or any primitive cell of the reciprocal lattice)
- Any $\mathbf{k}'$ not in the first Brillouin zone can be written as: $\mathbf{k}' = \mathbf{k} + \mathbf{K}$, where $\mathbf{k}$ is in the first Brillouin zone and $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$
- The labels K,L,W,X and Γ are high symmetry points in the Brillouin zone

Integrating Over The First Brillouin Zone



- Observables are calculated as integrals over all k-points within the first Brillouin zone:

$$\boxed{E_{\text{tot}} = \frac{1}{V_{\text{BZ}}} \int_{1^{\text{st}}\text{BZ}} E(\mathbf{k}) d\mathbf{k}}$$

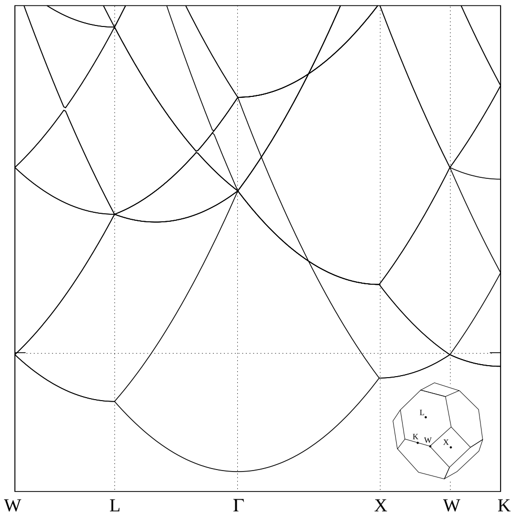
$$\boxed{n(\mathbf{r}) = \frac{1}{V_{\text{BZ}}} \int_{1^{\text{st}}\text{BZ}} n_{\mathbf{k}}(\mathbf{r}) d\mathbf{k}}$$

- The integrals for metals are more difficult to converge

Defining the k-Point Grid

- The standard method is the Monkhorst-Pack grid – a regular grid in k-space:
  Monkhorst, Pack. Phys. Rev. B **13** *p.5188 (1976)*
- The symmetry of the cell can be used to reduce the number of k-points needed to obtain convergence
- Shifting the origin of the grid can improve the convergence with the number of k-points
- The larger the unit cell used, generally the fewer k-points that are required to acheive convergence (but there are more bands)

Band Structure



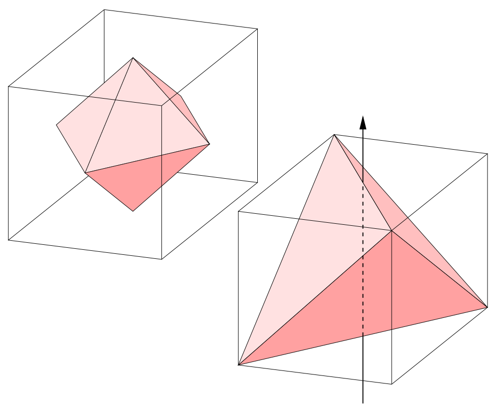
FCC free electron bandstructure

- For a given $\mathbf{k}$ there many solutions to the Schrödinger equation: $H_{\mathbf{k}} u_{\mathbf{k}} = E_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}), u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R})$

- The boundary conditions ensure that there are many (labelled n) discretely spaced eigenvalues

- The Hamiltonian depends on $\mathbf{k}$ as a parameter, and so the eigenvalues vary continuously with wave vector for a given n. Hence, they are *bands*

Beyond Translational Symmetry in Crystals



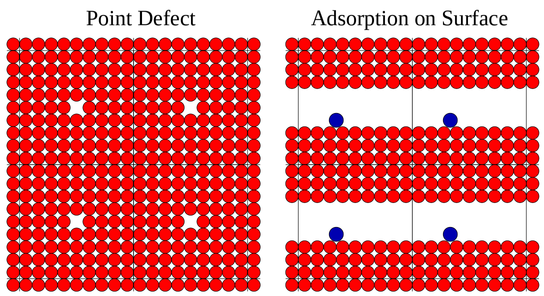
The symmetries of a cube are identical to an octahedron, but not a tetrahedron

- There can be other symmetries in addition to translational symmetry

- The subject of crystallography systematises the classification of these different symmetries

- The number of possibilities can be shown to be finite for crystals, and have been ennumerated

The Super-cell approximation



- Aperiodic systems can also be treated within periodic boundary conditions

- A cell is chosen that mimics the aperiodic behaviour, but the periodic boundary conditions remain

- This is the *super-cell*

- The super-cell chosen must be large enough that the properties of interest are converged with respect to cell size