

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 $n(\mathbf{r})$:
- But, just as for the $E_{xc}[n]$ we don't know what this functional $T[n]$ is.

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

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

THE KOHN-SHAM EQUATIONS

$$\begin{aligned} E_{\text{tot}}[\{\psi_i\}] &= -2 \sum_i \frac{\hbar^2}{2m} \int \psi_i \nabla^2 \psi_i d\mathbf{r} \\ &+ \int V_{\text{ion}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \\ &+ \frac{e^2}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &+ E_{\text{xc}}[n(\mathbf{r})] + E_{\text{ion}}(\mathbf{R}_i) \end{aligned}$$

The charge density is written as:

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

The potentials are given by *functional* derivatives:

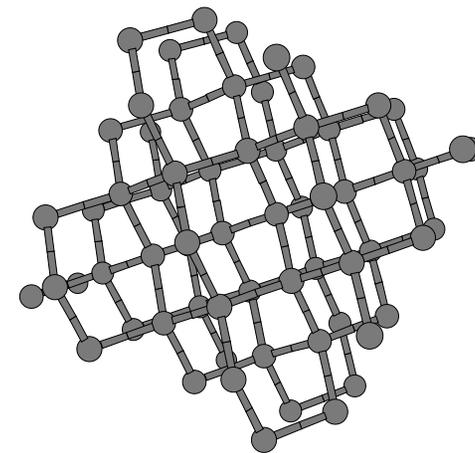
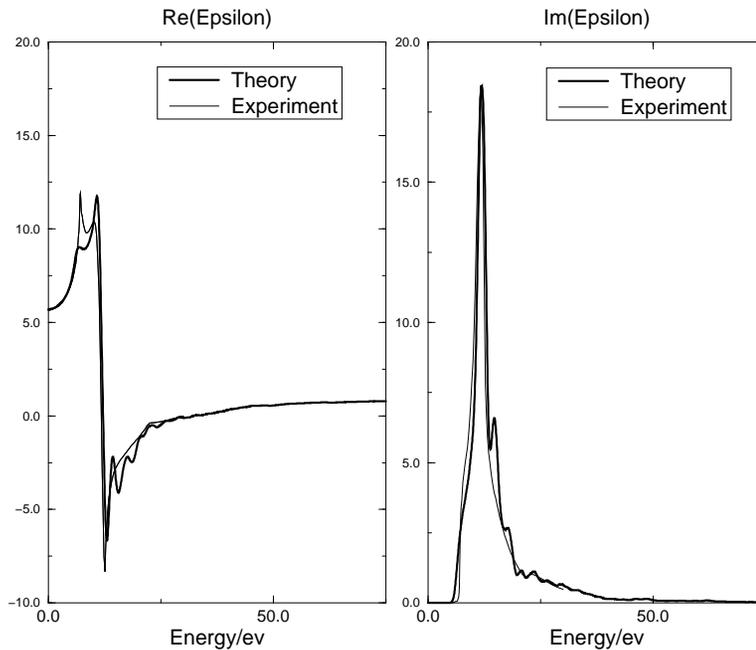
$$V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \text{ etc.}$$

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

THE KOHN-SHAM ORBITALS

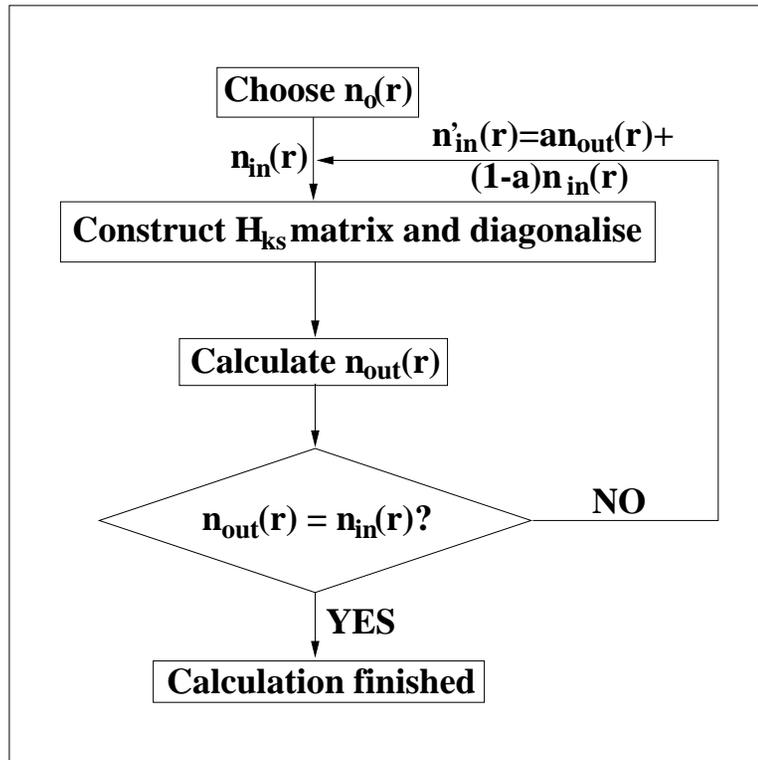
- The Kohn-Sham orbitals were introduced so that we can compute the independent electron kinetic energy corresponding to a charge density $n(\mathbf{r})$
- They need not have any physical meaning, nor need the Kohn-Sham eigenvalues
- However, experience shows that they do have some correspondence to 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:

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

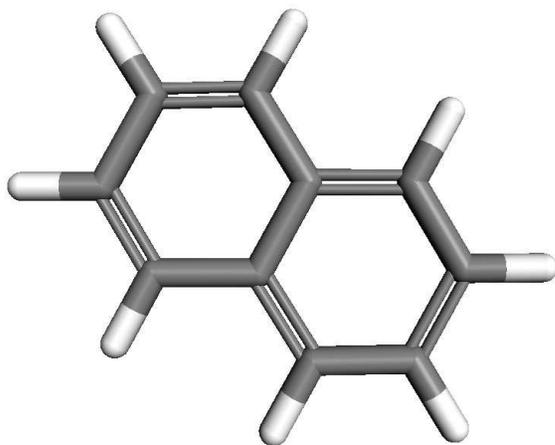
- If we choose a basis, we can construct a Hamiltonian as a matrix and diagonalise that matrix to get the eigenvectors and eigenvalues:

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

energy level \rightarrow eigenvalue

wavefunction \rightarrow eigenvector

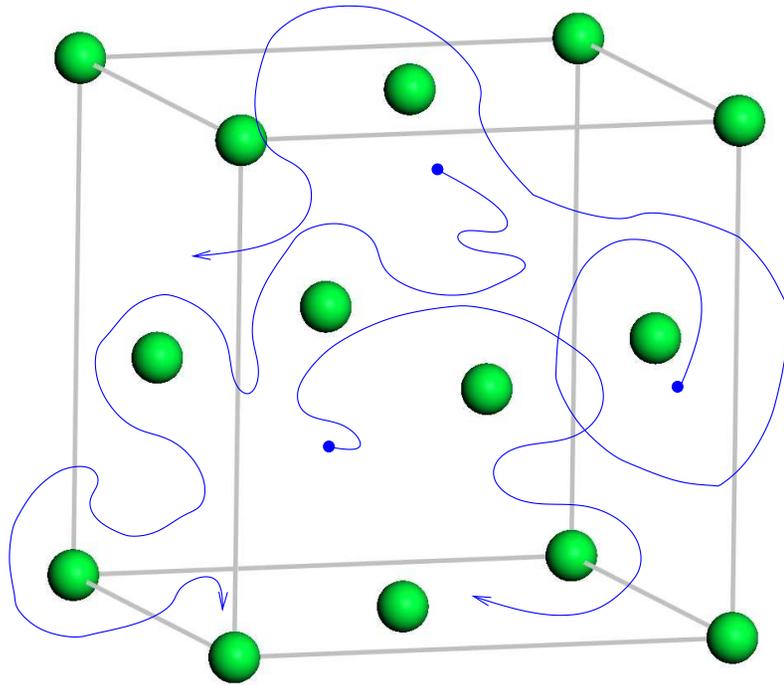
JUST A FEW ATOMS



Naphthalene

- 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 $O(N^3)$

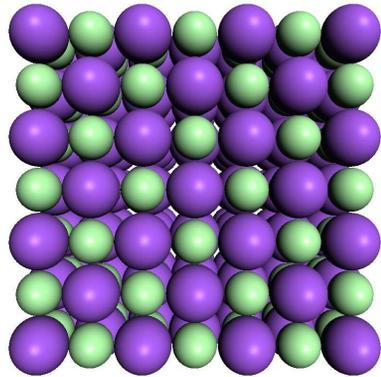
ELECTRONS IN CRYSTALS



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 — 1\AA — 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

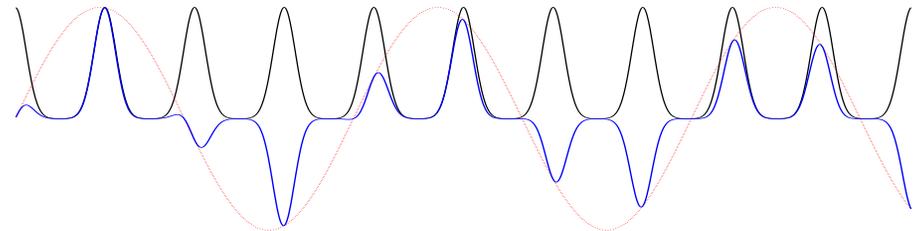
PERIODIC BOUNDARY CONDITIONS AND BLOCH'S THEOREM

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

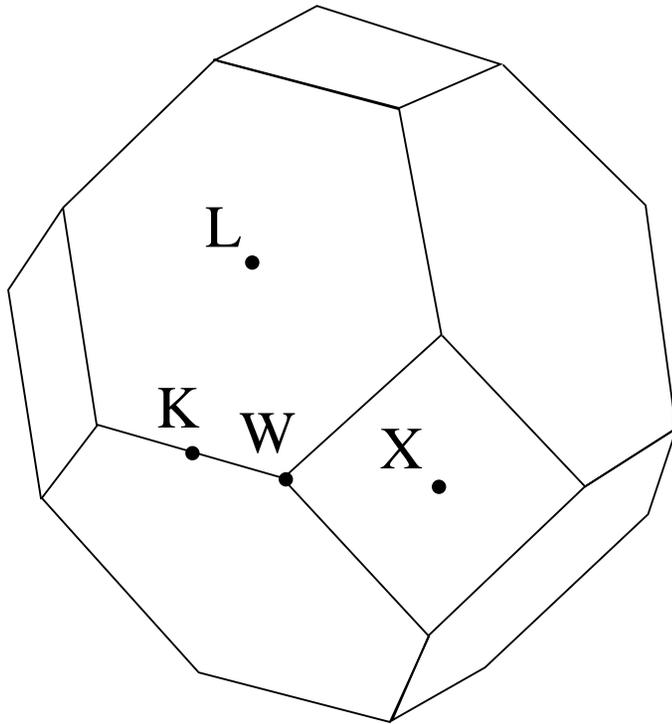
$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

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

- 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



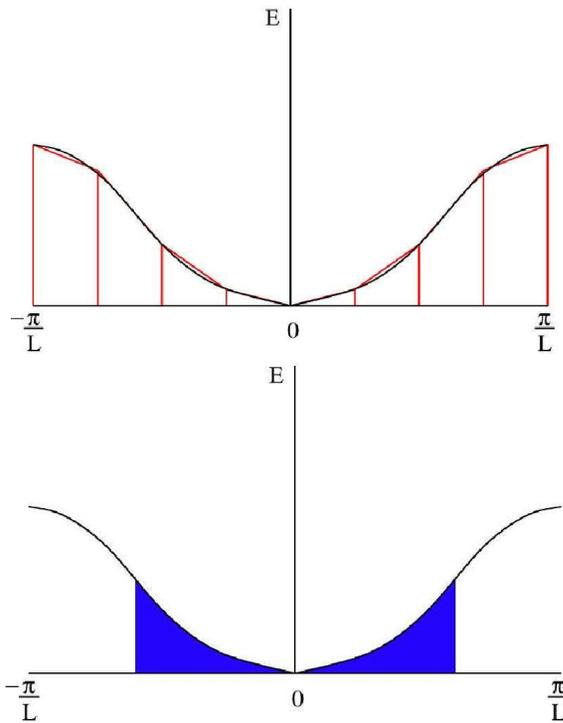
THE FIRST BRILLOUIN ZONE



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:

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

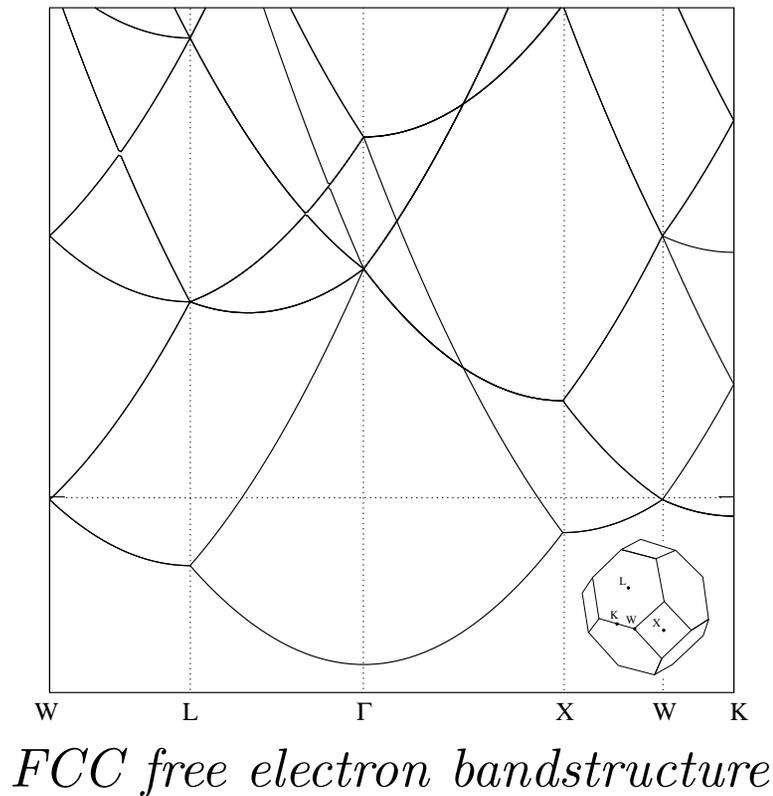
$$n(\mathbf{r}) = \frac{1}{V_{\text{BZ}}} \int_{1^{\text{st}}\text{BZ}} n_{\mathbf{k}}(\mathbf{r}) d\mathbf{k}$$

- The integrals for metals are more difficult to converge

DEFINING THE K-POINT GRID

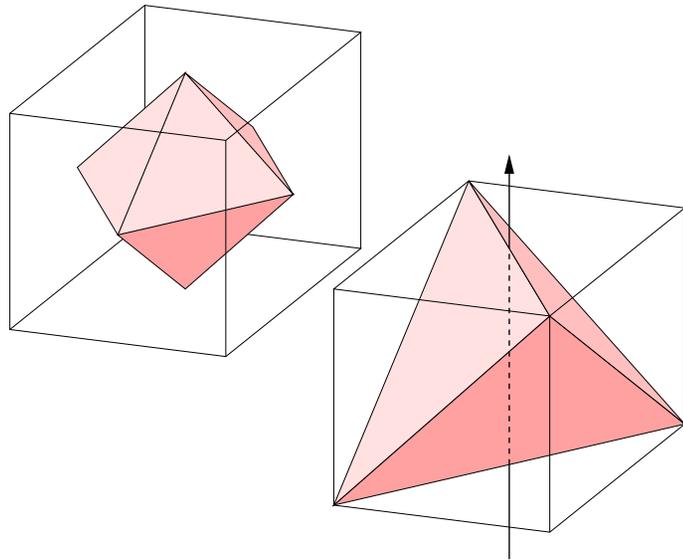
- The standard method is the Monkhorst-Pack grid – a regular grid in k-space:
Monkhorst, Pack. Phys. Rev. B **13** p.5188 (1976)
- The symmetry of the cell can be used to reduce the number of k-points needed to obtain convergence
- Shifting the origin of the grid can improve the convergence with the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

BAND STRUCTURE



- For a given \mathbf{k} there are 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*

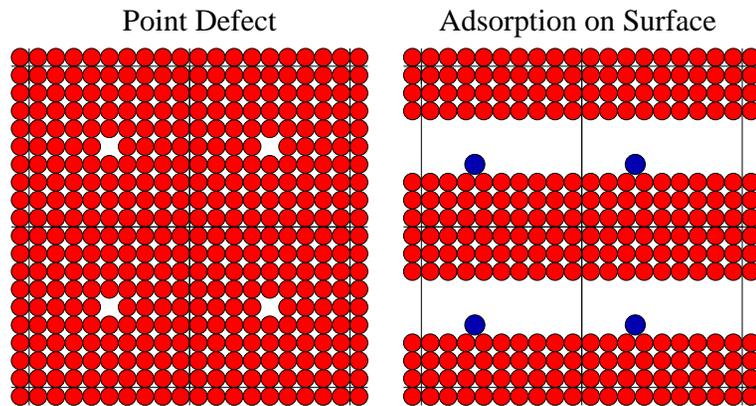
BEYOND TRANSLATIONAL SYMMETRY IN CRYSTALS



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 enumerated

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