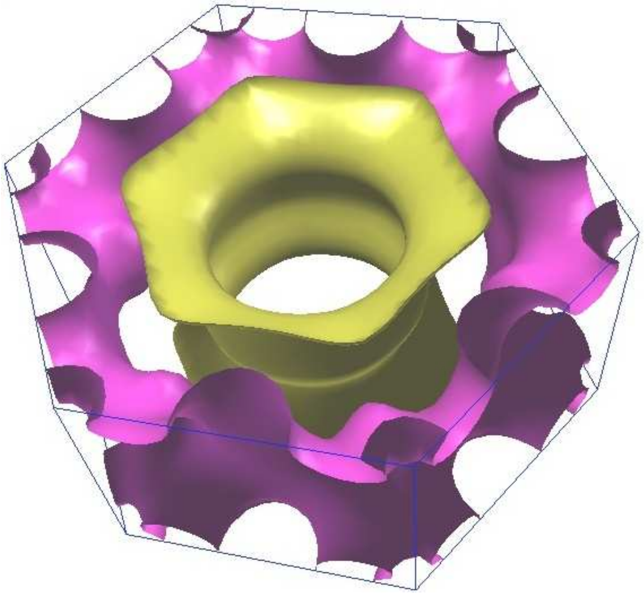
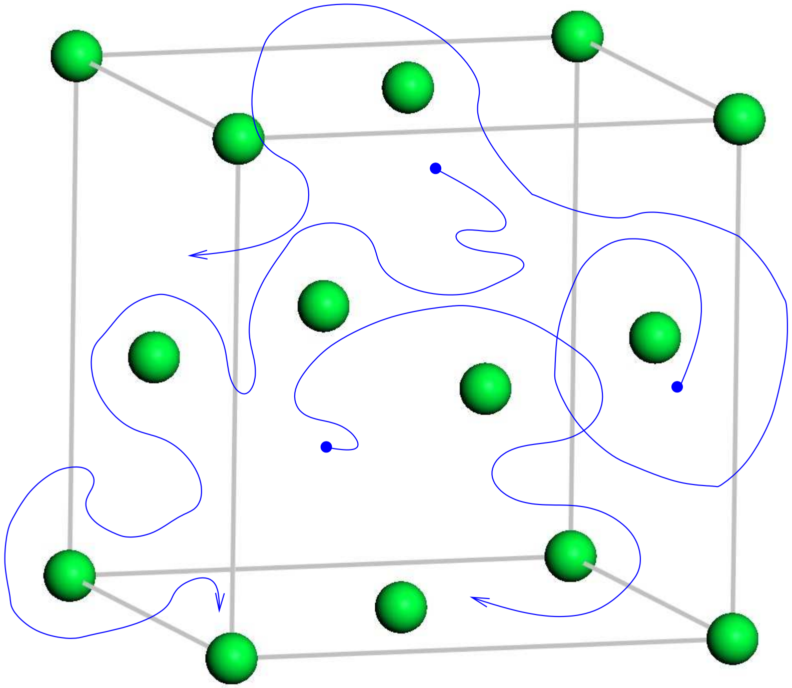
Electrons in Crystals

Chris J. Pickard



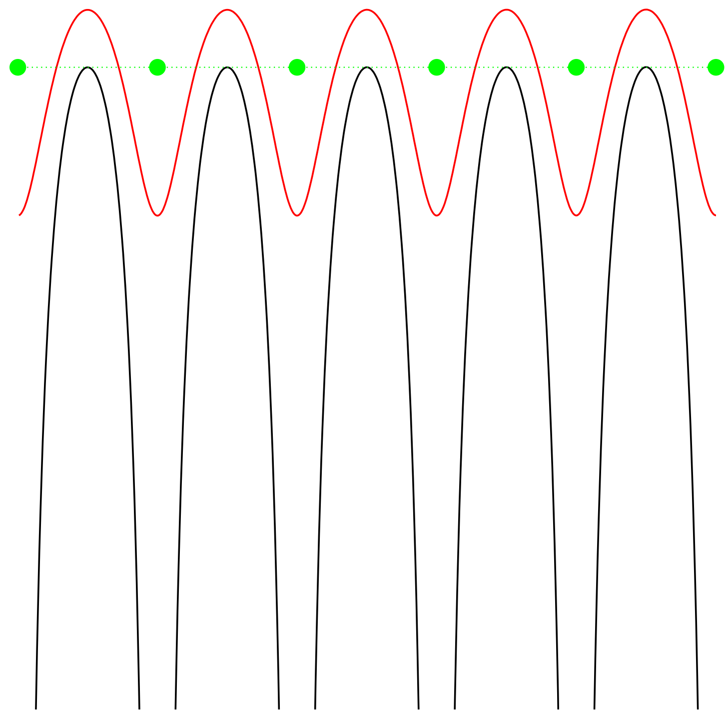
ELECTRONS IN CRYSTALS



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

THE PERIODIC POTENTIAL



A 1D periodic crystalline potential

- In principle, we are faced with a many electron problem

- But we can make a lot of progress using the *independent electron* approximation

- We investigate the properties of the Schrödinger equation for a single electron:
  $H\Psi = (-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}))\Psi = E\Psi$
  with $U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r})$

BLOCH'S THEOREM

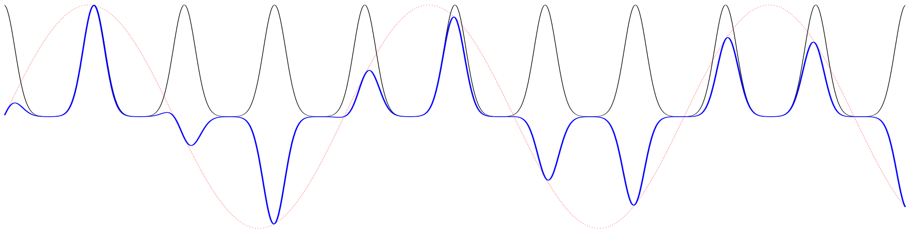
$$\boxed{\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})}$$

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

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

- 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



PROOF OF BLOCH'S THEOREM

Consider the translation operator:

$$T_{\mathbf{R}} f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R})$$

It forms a commuting set for all $\mathbf{R}$ and H:

$$T_{\mathbf{R}} H \Psi(\mathbf{r}) = H(\mathbf{r} + \mathbf{R}) \Psi(\mathbf{r} + \mathbf{R}) = H(\mathbf{r}) \Psi(\mathbf{r} + \mathbf{R}) = H T_{\mathbf{R}} \Psi(\mathbf{r})$$

$$T_{\mathbf{R}} H = H T_{\mathbf{R}}$$

$$T_{\mathbf{R}} T_{\mathbf{R}'} = T_{\mathbf{R}'} T_{\mathbf{R}} = T_{\mathbf{R}+\mathbf{R}'}$$

The eigenstates of H are simultaneous eigenstates of all $T_{\mathbf{R}}$:

$$H\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

$$T_{\mathbf{R}}\Psi(\mathbf{r}) = c(\mathbf{R})\Psi(\mathbf{r})$$

The properties of $T_{\mathbf{R}}$ imply a relationship between the eigenvalues:

$$T_{\mathbf{R}}T_{\mathbf{R}'}\Psi(\mathbf{r}) = c(\mathbf{R})T_{\mathbf{R}'}\Psi(\mathbf{r}) = c(\mathbf{R})c(\mathbf{R}')\Psi(\mathbf{r})$$

$$T_{\mathbf{R}}T_{\mathbf{R}'}\Psi(\mathbf{r}) = T_{\mathbf{R}+\mathbf{R}'}\Psi(\mathbf{r}) = c(\mathbf{R}+\mathbf{R}')\Psi(\mathbf{r})$$

and so:

$$c(\mathbf{R})c(\mathbf{R}') = c(\mathbf{R}+\mathbf{R}')$$

If $\mathbf{a}_i$ are the primitive lattice vectors, we can always write:

$$c(\mathbf{a}_i) = e^{2\pi i x_i}$$

For an arbitrary Bravais lattice vector:

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

and so, considering repeated applications of $T_{\mathbf{a}_i}$:

$$c(\mathbf{R}) = c(\mathbf{a}_1)^{n_1} c(\mathbf{a}_2)^{n_2} c(\mathbf{a}_3)^{n_3} = e^{i\mathbf{k}\cdot\mathbf{R}}$$

where $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$ and $\mathbf{k} = x_1\mathbf{b}_1 + x_2\mathbf{b}_2 + x_3\mathbf{b}_3$

We arrive at the second form of Bloch's Theorem:

$$\boxed{T_{\mathbf{R}}\Psi(\mathbf{r}) = \Psi(\mathbf{r}+\mathbf{R}) = c(\mathbf{R})\Psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}}\Psi(\mathbf{r})}$$

Born-von Karman Boundary Conditions

Apply periodic BCs to a commensurate supercell:

$$\Psi(\mathbf{r} + N_i\mathbf{a}_i) = \Psi(\mathbf{r}),\ \ i = 1, 2, 3$$

and then Bloch's theorem:

$$\Psi_{n\mathbf{k}}(\mathbf{r} + N_i\mathbf{a}_i) = e^{iN_i\mathbf{k}\cdot a_i}\Psi_{n\mathbf{k}}(\mathbf{r})$$

$$e^{iN_i\mathbf{k}\cdot\mathbf{a}_i} = e^{2\pi i N_i x_i} = 1$$

which means that $x_i = m_i/N_i$

The allowed Bloch wave vectors are:

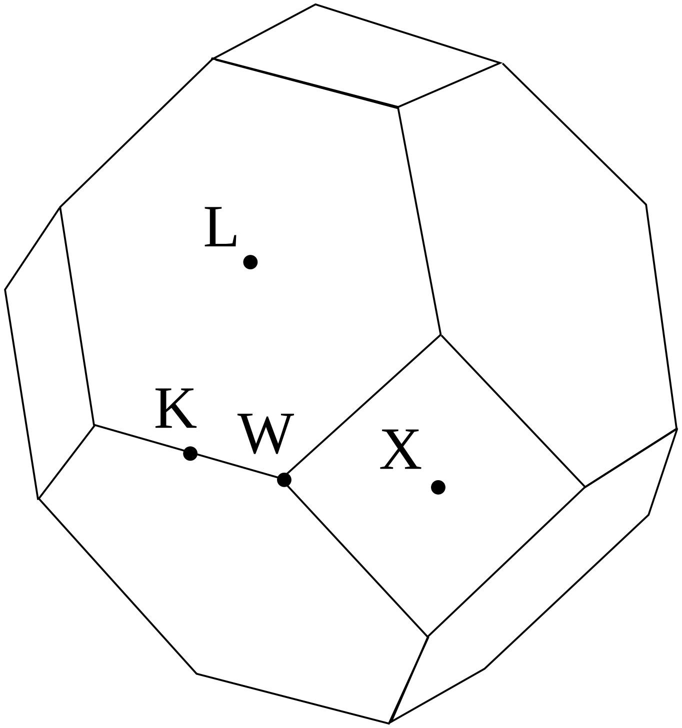
$$\mathbf{k} = \sum_{i=1}^{3} \frac{m_i}{N_i}\mathbf{b}_i$$

and the volume $\Delta\mathbf{k}$ of k-space per $\mathbf{k}$:

$$\Delta\mathbf{k} = \frac{1}{N}\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = \frac{(2\pi)^3}{V}$$

The number of allowed k-vectors in the primitive cell of the reciprocal lattice is equal to the number of cells in the crystal

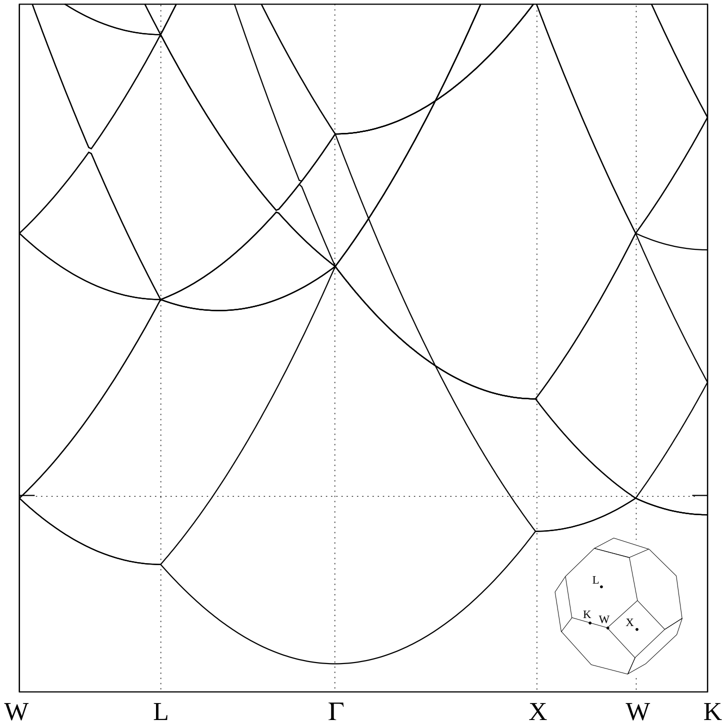
THE FIRST BRILLOUIN ZONE



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

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 condition 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*

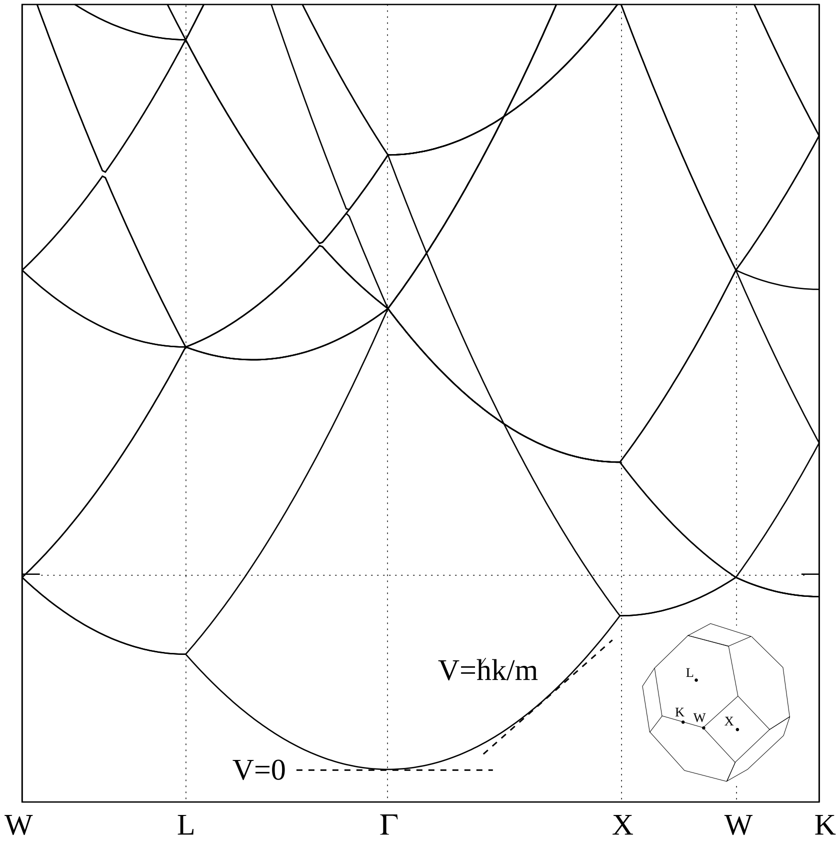
CRYSTAL MOMENTUM

- For Bloch electrons $\mathbf{k}$ is not proportional to electronic momentum

$$\begin{aligned}\frac{\hbar}{i}\nabla\Psi_{n\mathbf{k}} &= \frac{\hbar}{i}\nabla(e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})) \\ &= \hbar\mathbf{k}\Psi_{n\mathbf{k}} + e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\hbar}{i}\nabla u_{n\mathbf{k}}\end{aligned}$$

- The $\Psi_{n\mathbf{k}}$ are not momentum eigenstates
- However, $\hbar\mathbf{k}$ is a natural extension of $\mathbf{p}$, and known as *crystal momentum*
- The dynamical significance of $\hbar\mathbf{k}$ is revealed by considering electrons response to applied electromagnetic fields
- A quantum number characteristic of the translational symmetry of the periodic potential, as $\mathbf{p}$ is characteristic of the full translational symmetry of free space

Velocity and Effective Mass



- The velocity of an electron at $\mathbf{k}$ in band n is given by the gradient of the band and the inverse effective mass is given by the curvature

- The velocity operator is:
$$\mathbf{v} = d\mathbf{r}/dt = (1/i\hbar)[\mathbf{r}, H] = \mathbf{p}/m$$
$$= \hbar\nabla/im$$

- Electrons in a perfect crystal move at a constant mean velocity

DENSITY OF STATES

- Many electronic properties are weighted sums over the electronic levels of the form:
  $Q = 2\sum_{n\mathbf{k}} Q_n(\mathbf{k})$
  which is an integral in a large crystal:
  $q = 2\sum_n \int \frac{d\mathbf{k}}{(2\pi)^3} Q_n(\mathbf{k})$

- Often $Q_n(\mathbf{k})$ depends only on n and $\mathbf{k}$ through $E_n(\mathbf{k})$, and the *density of states* $g(E) = \sum_n g_n(E)$ is a useful construct:
  $q = \int dE g(E) Q(E)$

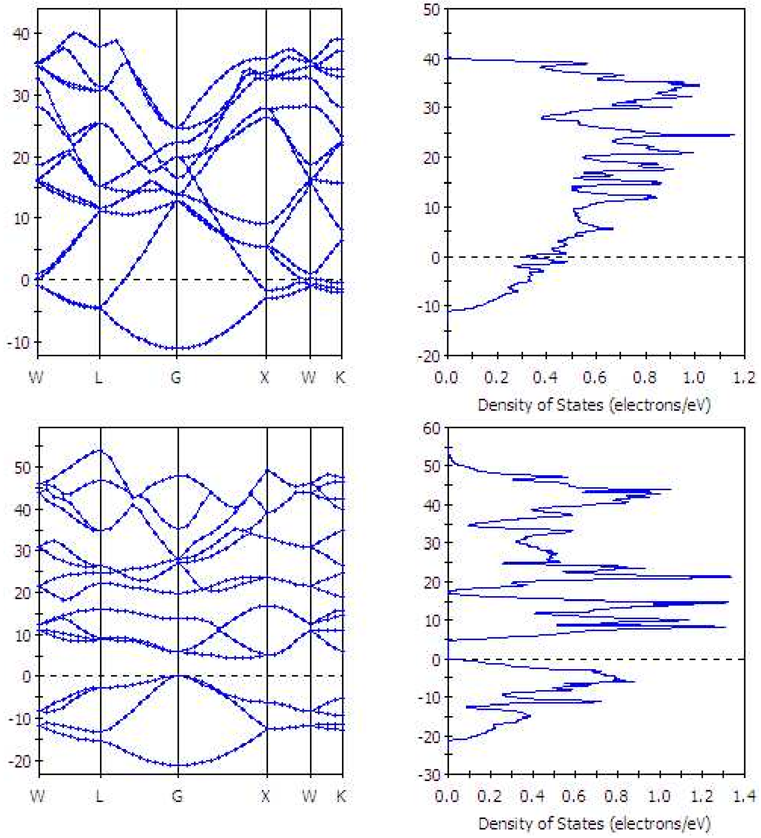
- The density of states of a band is:
  $$\boxed{g_n(E) = \int \frac{d\mathbf{k}}{4\pi^3} \delta(E - E_n(\mathbf{k}))}$$

- It can be written as a surface integral:
  $$\boxed{g_n(E) = \int_{S_n(E)} \frac{dS}{4\pi^3} \frac{1}{|\nabla E_n(\mathbf{k})|}}$$
  with $S_n(E)$ a surface of constant energy

VAN HOVE SINGULARITIES

- Because $E_n(\mathbf{k})$ is periodic in reciprocal space, and for each n bounded from above an below, and differentiable everywhere there must be $\mathbf{k}$ for which $|\nabla E| = 0$
- Thus, the integrand in the expression for $g_n(E)$ diverges
- In 1D this results in a divergence of the density of states itself
- In 3D the divergence is integrable, and results in discontinuities in dg_n/dE
- These are the *van Hove singularities*

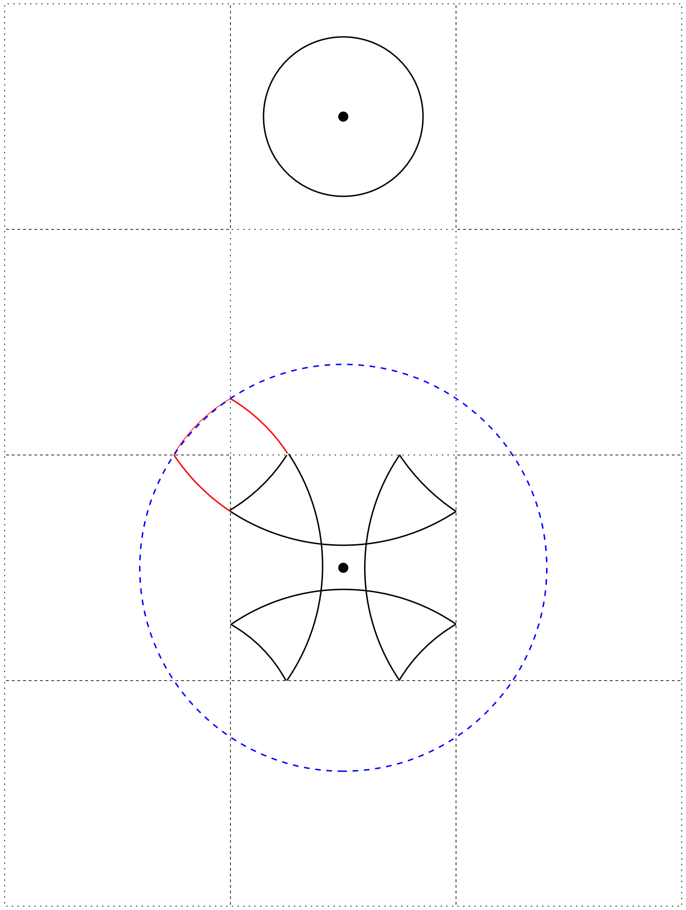
METALS AND INSULATORS



- Fill the electronic states, lowest energy first across the whole first Brillouin zone (so that each level is counted only once), until all the electons are accomodated

- If there is a *gap* between the highest occupied state and the lowest unoccupied the crystal is an *insulator* (and a called a *semiconductor* if the gap is close to $k_B T$)

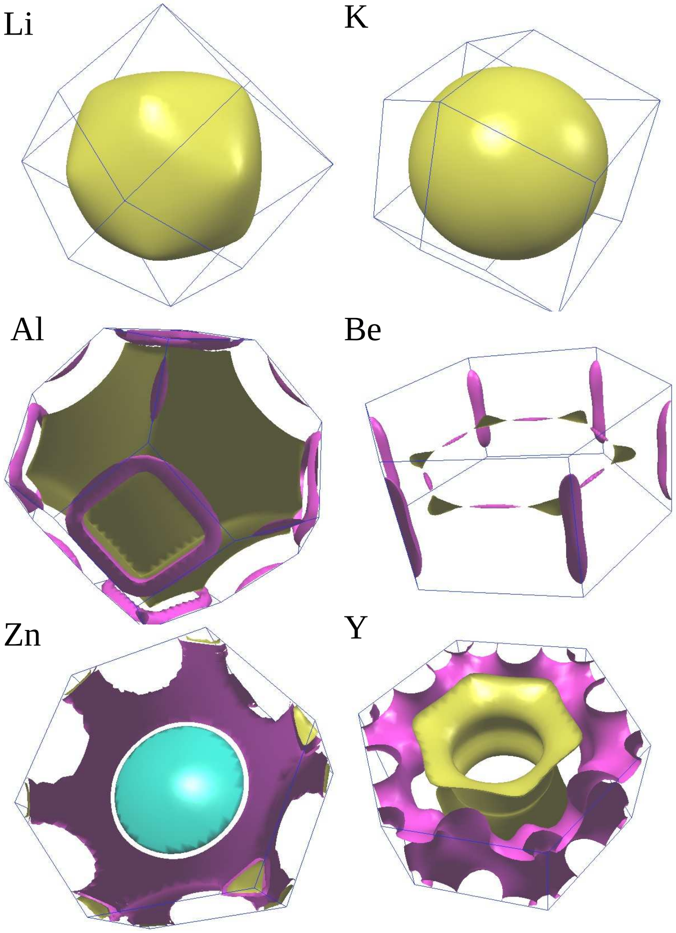
THE FERMI SURFACE



- If there is no gap then the crystal is a metal

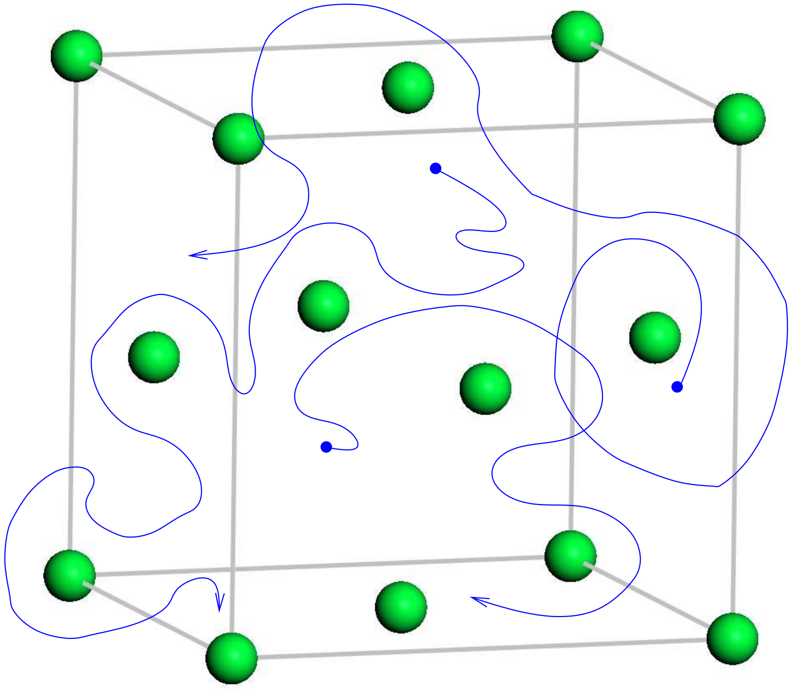
- There will be a surface in k-space separating occupied from unoccupied levels: this is known as the *Fermi surface* and may consist of several *branches*. It determines the transport and optical properties of the metal

The Fermi Surface



- If there is no gap then the crystal is a metal
- There will be a surface in k-space separating occupied from unoccupied levels: this is known as the *Fermi surface* and may consist of several *branches*. It determines the transport and optical properties of the metal

ELECTRONS IN A REALISTIC CRYSTAL POTENTIAL

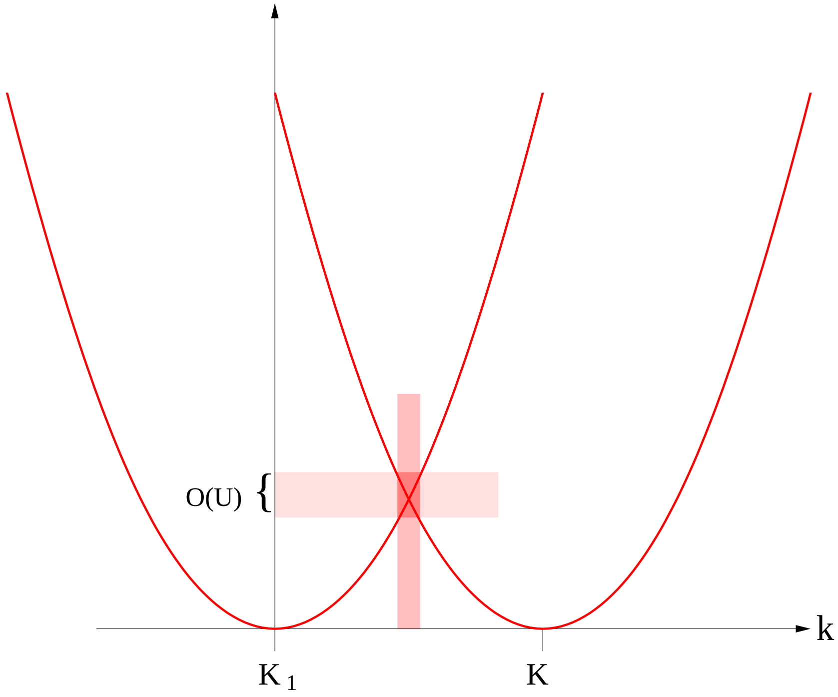


- In principle, it remains only to solve the Schrödinger's equation for the Bloch wavefunctions

- This might be viewed as a job of pure numerics – aside from the choice of $U(\mathbf{r})$

- But we can do better than brute force – and with greater understanding

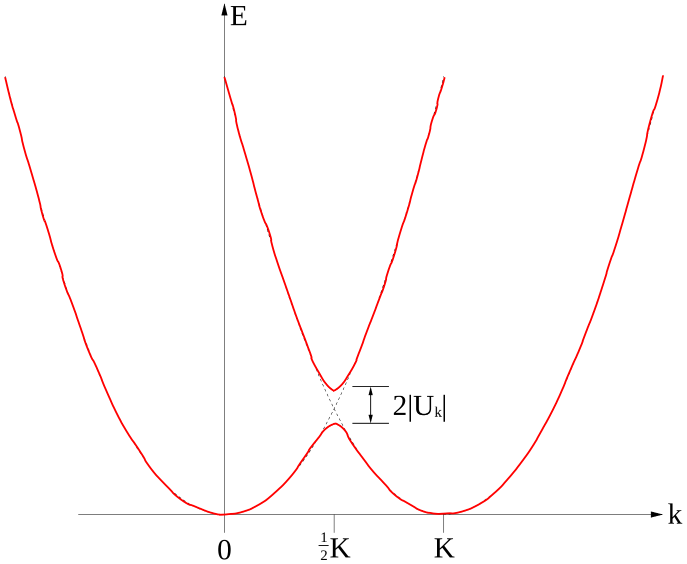
THE NEARLY FREE ELECTRON APPROXIMATION



Defining near degeneracy

- Possibly suprisingly, the electronic structure of some metals is considered to arise from a weak periodic perturbation of the free electron gas
- This is due to the combined effects of the Pauli exclusion principle and *screening*
- The perturbation has different results, depending whether the free electron states are nearly degenerate or not

The Nearly Free Electron Approximation



Splitting at a single Bragg plane

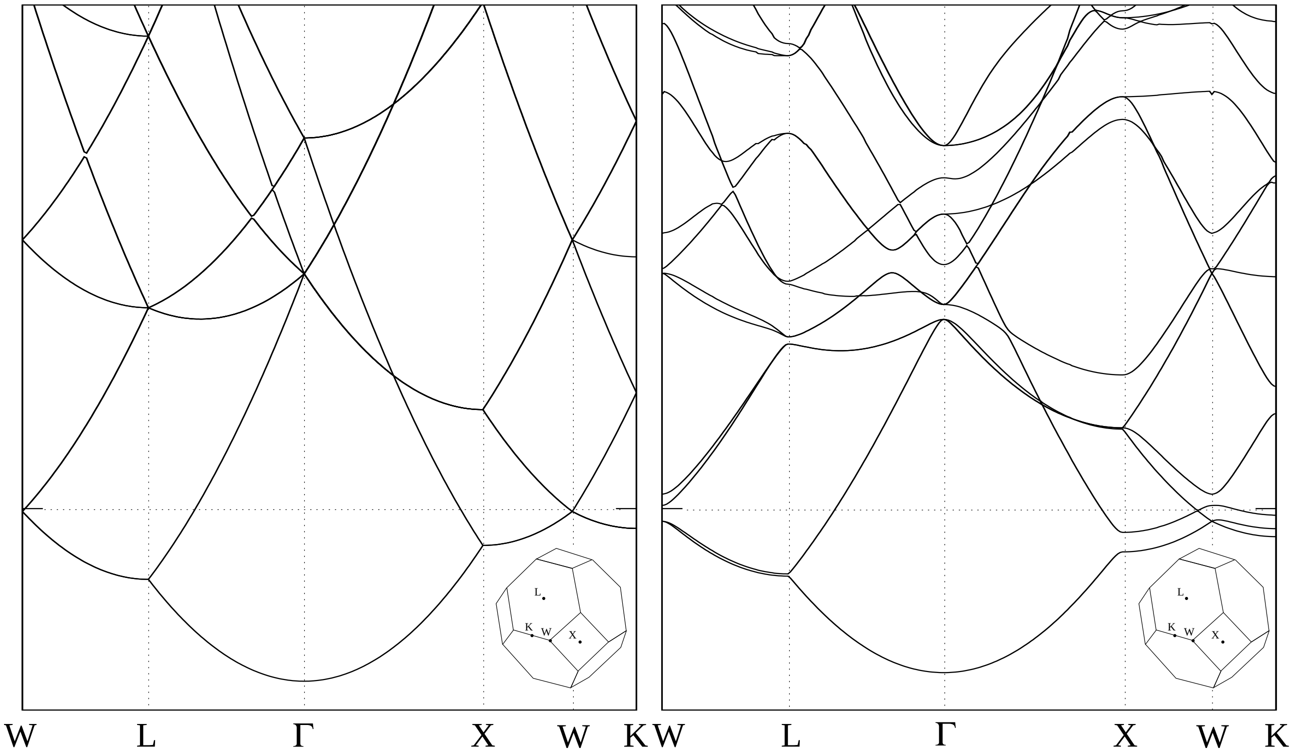
- If there is no degeneracy, the pertubation is second order in $U_{\mathbf{K}}$

- If there is near degeneracy, the perturbation can be linear in the potential

- Symmetries and structure factor effects can eliminate the splitting – returns with *spin-orbit coupling*

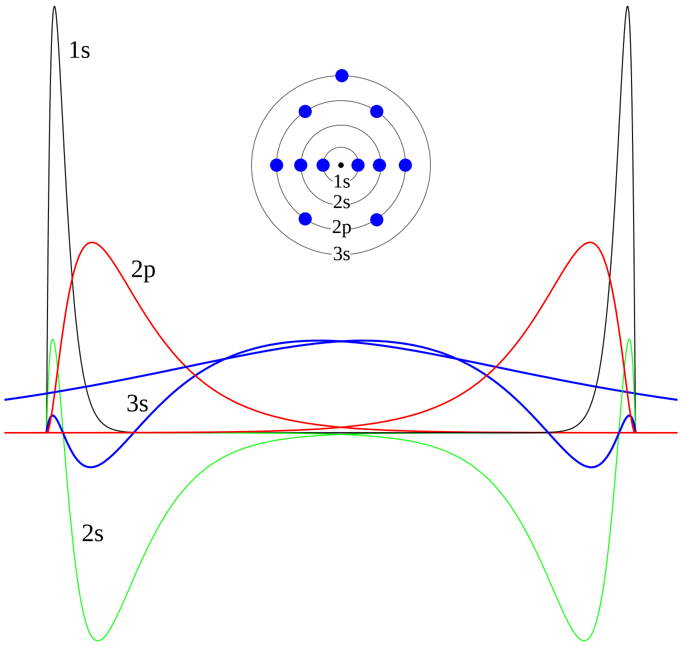
- The bandstructure can be plotted in the *reduced* or *extended* or *repeated* zone schemes

Free electron and a Real Bandstructure



The free electron and DFT bandstructure of FCC Aluminium

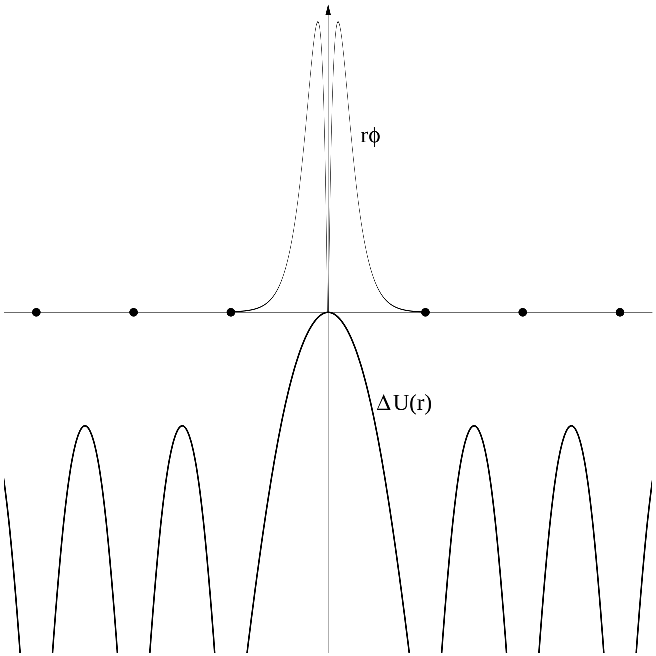
THE TIGHT BINDING APPROXIMATION



Sodium electronic wavefunctions – separated by 3.7Å

- Now, let's think of the electronic structure as being a modification of that of the isolated constituent atoms
- This is a good picture if the overlap of the atomic wavefunctions is small
- Clearly, this is not the case for metallic sodium – it is a nearly free electron metal

The Tight Binding Approximation



When $r\phi(\mathbf{r})$ *is large,* $\Delta U(\mathbf{r})$ *is small and vice versa*

- To calculate the corrections, consider: $H = H_{\mathrm{at}} + \Delta U(\mathbf{r})$
- The general form of the wavefunction is: $\psi(r) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\phi(\mathbf{r}-\mathbf{R})$ where $\phi(\mathbf{r}) = \sum_n b_n \psi_n(\mathbf{r})$
- There is a strong *hybridisation* and splitting of levels close to each other in energy – recall the nearly free electron model

THE TIGHT BINDING S-BAND

Consider a single s-band: $|\psi_{\mathbf{k}}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}|\psi_{\mathrm{s}}\rangle$

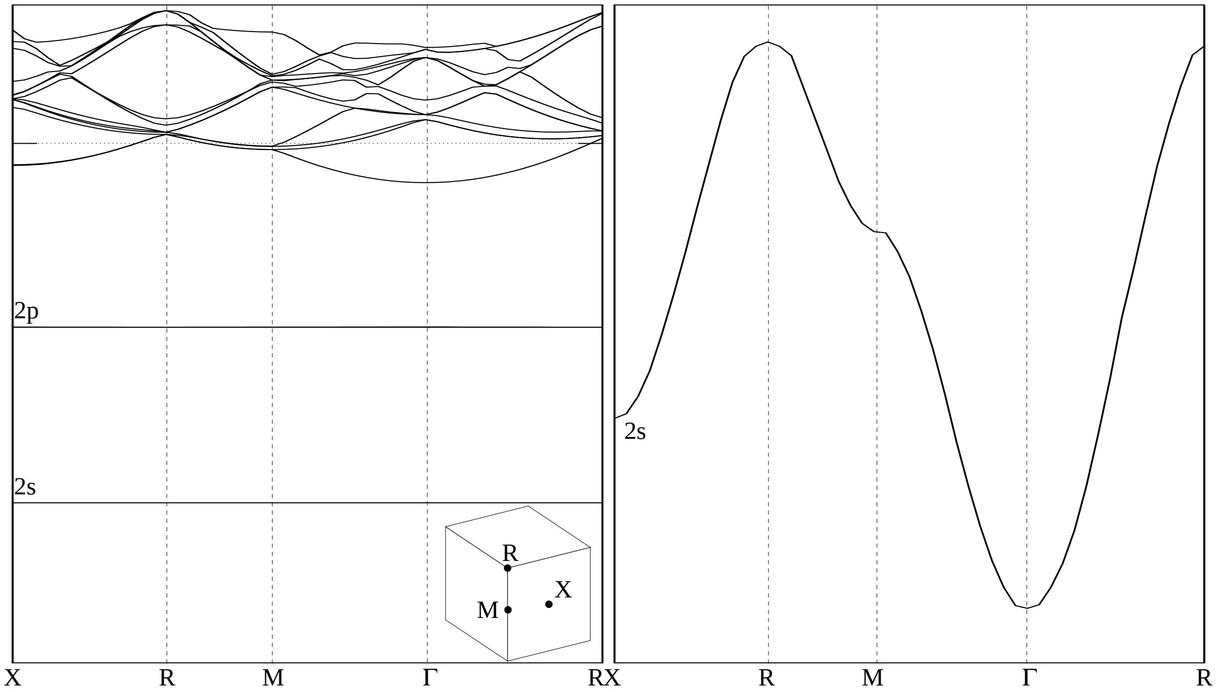
Multiply: $H|\psi_{\mathbf{k}}\rangle = (H_{\mathrm{at}} + \Delta U)|\psi_{\mathbf{k}}\rangle = \mathcal{E}_{\mathbf{k}}|\psi_{\mathbf{k}}\rangle$ through by $\langle\psi_s|$ and integrate using $\langle\psi_{\mathrm{s}}|H_{\mathrm{at}}|\psi_{\mathrm{s}}\rangle = E_s$:

$(\mathcal{E}_{\mathbf{k}} - E_s)\langle\psi_s|\psi_{\mathbf{k}}\rangle = \langle\psi_s|\Delta U|\psi_{\mathbf{k}}\rangle \Rightarrow \mathcal{E}_{\mathbf{k}} = E_s + \frac{\langle\psi_s|\Delta U|\psi_{\mathbf{k}}\rangle}{\langle\psi_s|\psi_{\mathbf{k}}\rangle}$

Ignoring the devations from unity of the denominator, summing over the nearest neighbours only, and using the inversion symmetry of the potential:

$$\boxed{\mathcal{E}_{\mathbf{k}} = E_s + \langle\psi_s|\Delta U|\psi_s\rangle + \sum_{nn}\cos(\mathbf{k}\cdot\mathbf{R})\int \psi_s^*(\mathbf{r})\Delta U(\mathbf{R})\psi_s(\mathbf{r}-\mathbf{R})d\mathbf{r}}$$

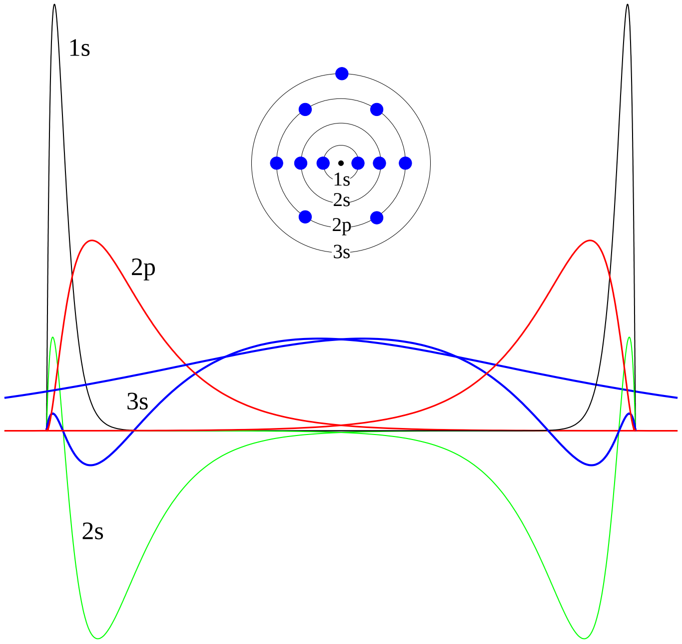
THE TIGHT BINDING s-BAND



Sodium in a Simple Cubic cell of side 3.7Å:

$$\mathcal{E}_{\mathbf{k}} = \alpha - \beta(\cos\ ak_x + \cos\ ak_y + \cos\ ak_z)$$

VALENCE BAND WAVEFUNCTIONS



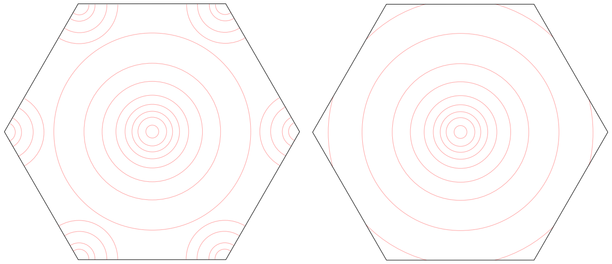
Sodium electronic wavefunctions – separated by 3.7Å

- All electonic structure methods must face up to a truth: the valence wavefunctions are difficult to describe in any one way

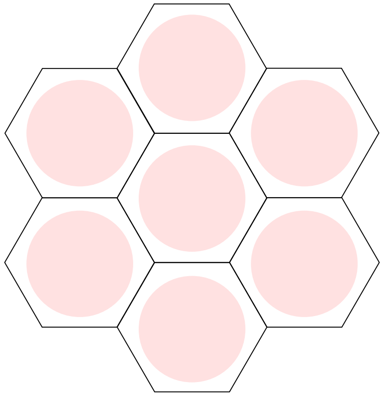
- They are smooth in the interstitial regions, and oscillatory in the core regions

- This is because the valence wavefunctions must be orthogonal to the core states

ELECTRONIC STRUCTURE METHODS



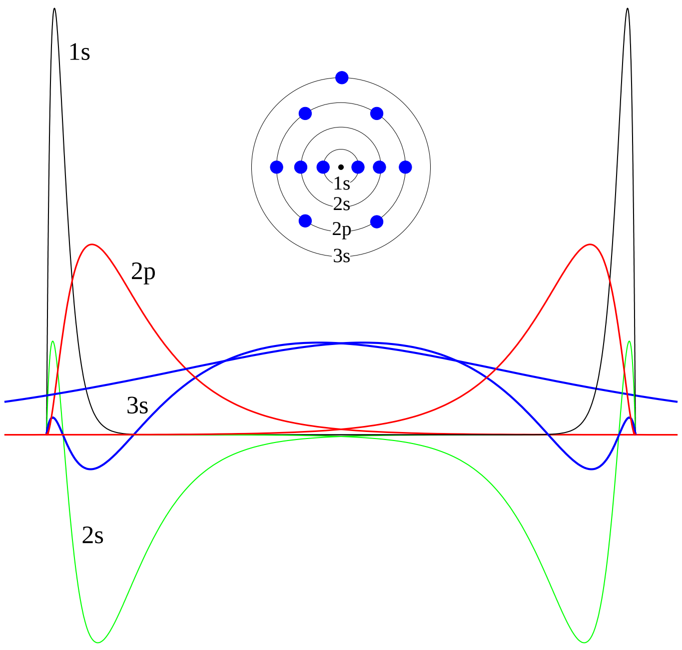
The Cellular potential



The Muffin Tin potential

- The Cellular method
- The Augmented Plane-wave method (APW)
- The Green's Function method (KKR)
- The Orthogonalised Plane-wave method (OPW)

THE PSEUDOPOTENTIAL APPROACH

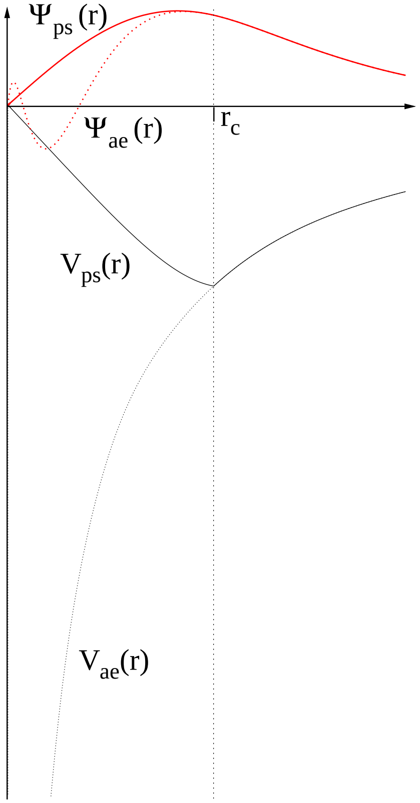


- The pseudopotential was originally thought of as the weaker effective potential due to the orthogonality of the valence to the core wavefunctions

- This concept provided a justification and theoretical framework for the nearly free electron approximation

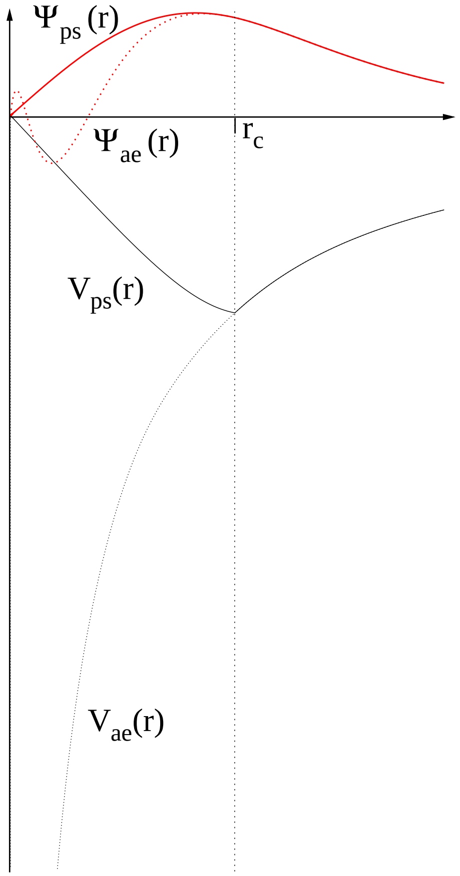
- The true power of the method unleashed by much later *ab initio* formulations

THE PSEUDOPOTENTIAL SCHEME



- Do an all electron atomic calculation
- Choose a core radius, and *pseudise* the atomic wavefunctions in the channels of interest
- The simplest schemes conserve the *norm* but this can be relaxed
- Invert the Schrödinger equation to find the *pseudopotential*

THE PSEUDOPOTENTIAL SCHEME



- The resulting pseudopotential will reproduce the *reference* eigenstates by construction, and is nonlocal in general

- *Transferability* is of great importance – the potentials should be tested extensively

- There may be *ghost states*

PROJECTOR AUGMENTED WAVES

- The Projector Augmented Wave approach puts pseudopotential theory on a firm theoretical footing

- It defines an operator $\mathcal{T}$ which maps pseudowavefunctions to the all electron wavefunctions: $|\Psi\rangle = \mathcal{T}|\tilde{\Psi}\rangle$

- This operator can be chosen to be the following: $\mathcal{T} = \mathbf{1} + \sum_{\mathbf{R},n}[|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle]\langle\tilde{p}_{\mathbf{R},n}|$

- The projectors are defined so that: $\langle\tilde{p}_{\mathbf{R},n}|\tilde{\phi}_{\mathbf{R}',m}\rangle = \delta_{\mathbf{R},\mathbf{R}'}\delta_{n,m}$

- Pseudo operators can be defined: $\tilde{O} = \mathcal{T}^{+}O\mathcal{T}$

$$\boxed{\tilde{O} = O + \sum_{\mathbf{R},n,m} |\tilde{p}_{\mathbf{R},n}\rangle[\langle\phi_{\mathbf{R},n}|O|\phi_{\mathbf{R},m}\rangle - \langle\tilde{\phi}_{\mathbf{R},n}|O|\tilde{\phi}_{\mathbf{R},m}\rangle]\langle\tilde{p}_{\mathbf{R},m}|}$$

DERIVING THE PSEUDO HAMILTONIAN

- The PAW scheme can be applied to the all electron Hamiltonian H

  $$\tilde{H} = \mathcal{T}^{+} H \mathcal{T} = \tfrac{1}{2}p^2 + V + |\tilde{p}\rangle[\langle\phi|\tfrac{1}{2}p^2 + V|\phi\rangle - \langle\tilde{\phi}|\tfrac{1}{2}p^2 + V|\tilde{\phi}\rangle]\langle\tilde{p}|$$

  add and subract $V - V^{\text{loc}}$ which is localised:

  $$\boxed{\tilde{H} = \tfrac{1}{2}\mathbf{p}^2 + V^{\text{loc}}(\mathbf{r}) + \textstyle\sum_{\mathbf{R}} V^{\text{nl}}_{\mathbf{R}}}$$

- An arbitary choice for the *local* potential $V^{\text{loc}}(\mathbf{r})$ is made and the nonlocal potential is of the form:

  $$V^{\text{nl}}_{\mathbf{R}} = \textstyle\sum_{n,m} |\tilde{p}_{\mathbf{R},n}\rangle a^{\mathbf{R}}_{n,m} \langle\tilde{p}_{\mathbf{R},m}|$$