Electronic Structure Methods

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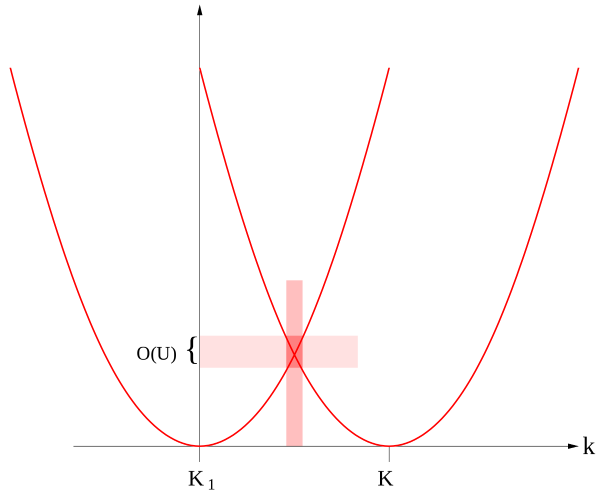
Lecture Six

An overview of the field

- There are many ways to try to solve the Schrödinder equation
- At the same level of theory (e.g. LDA DFT) all *should* give the same results
- The different methods amount to different numerical and computational choices and approximations
- Different methods have different strengths and weaknesses
  - some methods are fast, and scale well to large system sizes
  - some methods can take advantage of massively parallel super computers
  - some methods are very accurate
  - some work well for high symmetry situations, and others work well for high and low symmetry

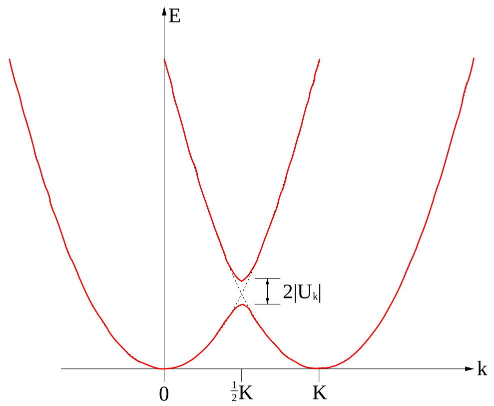
The Nearly Free Electron Approximation



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

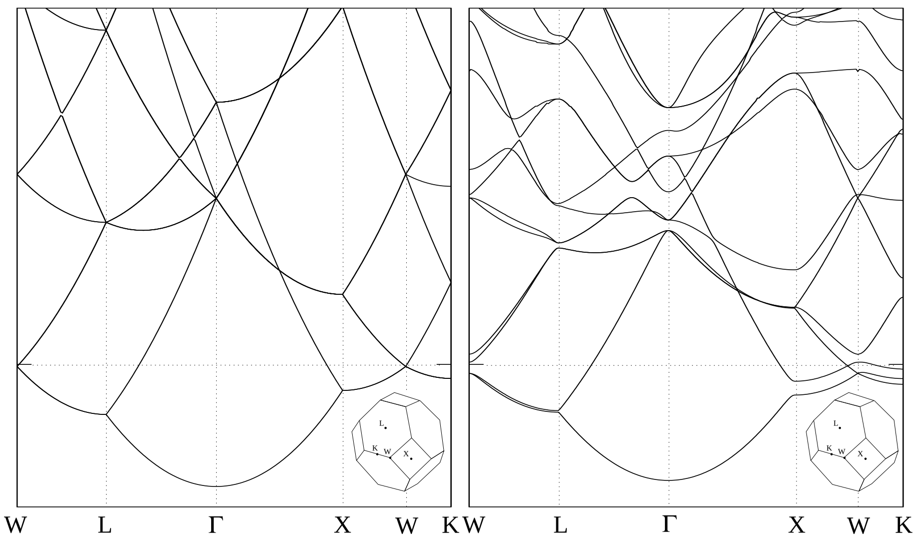
The Nearly Free Electron Approximation



Splitting at a single Bragg plane

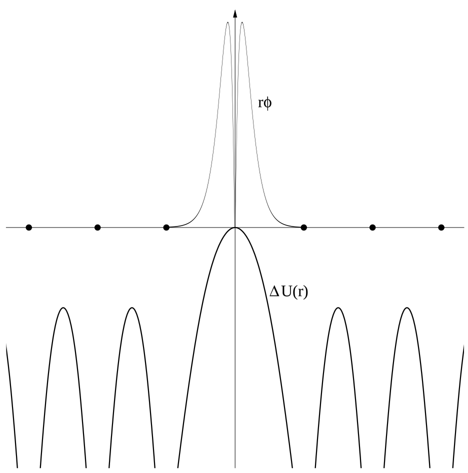
- If there is no degeneracy, the pertubation is second order in $U_{\mathbf{K}}$
- If there is near degeneracy, the perturbation can be linear in the potential
- Symmetries and structure factor effects can eliminate the splitting – returns with *spin-orbit coupling*
- The bandstructure can be plotted 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



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: $|\psi_{\mathbf{k}}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}|\psi_{\mathrm{s}}\rangle$

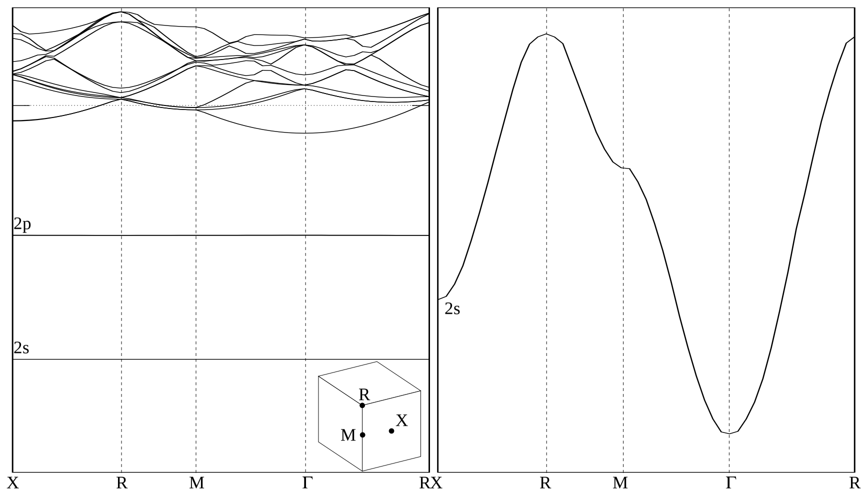
Multiply: $H|\psi_{\mathbf{k}}\rangle = (H_{\mathrm{at}} + \Delta U)|\psi_{\mathbf{k}}\rangle = \mathcal{E}_{\mathbf{k}}|\psi_{\mathbf{k}}\rangle$ through by $\langle\psi_s|$ and integrate using $\langle\psi_{\mathrm{s}}|H_{\mathrm{at}}|\psi_{\mathrm{s}}\rangle = E_s$:

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

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

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

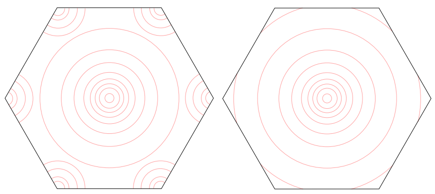
The Tight Binding s-Band



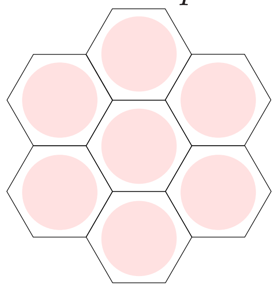
Sodium in a Simple Cubic cell of side 3.7Å:

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

Historical Electronic Structure Methods



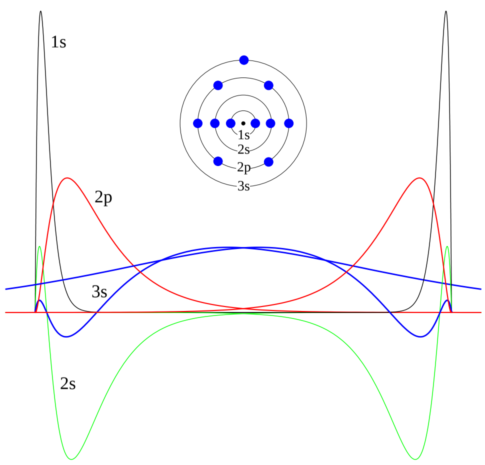
The Cellular potential



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 empirical pseudopotential method

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

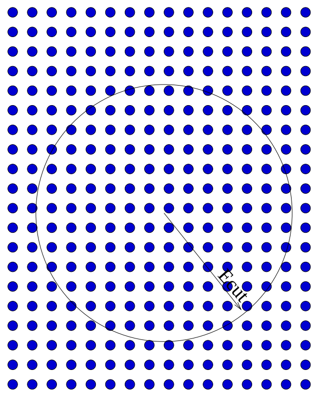
Modern Electronic Structure Methods

- Some of the traditional methods are still with us
  - linearized muffin tin orbitals (LMTO)
  - full potential linearized augmented plane wave (FLAPW)
- LMTO and FLAPW are all electron methods, and good for high symmetry compact structures, and heavy elements
- Pseudopotential based methods dominate

Planewaves: the natural basis set

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

- The natural basis set for a crystal
- PBCs lead to a discrete set
- Cutoff energy defines set - convergence well defined
- Advantages - FFTs, force calculation, orthogonality and simplicity
- Disadvantages - BIG



Operating with H on $|\psi_i\rangle$

- H divides into two parts
  - The potential — diagonal in real space
  - The kinetic energy — diagonal in reciprocal space
- Use FFTs — $N \ln N$ — and evaluate each term in appropriate space
- $V(\mathbf{r})$ in real space
- Kinetic energy in reciprocal space — $\frac{1}{2}|\mathbf{k}+\mathbf{G}|^2$

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: $\tilde{O} = \mathcal{T}^{+}O\mathcal{T}$

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

Quantum Chemical Approaches

- For many years the Quantum Chemical community relied on Hartree-Fock theory rather than DFT
  - better than LDA for molecules
  - but a disaster for metallic systems (hence restricted use in the physics community)
  - along with hybrid functionals such as B3LYP
- Quantum Chemical codes use local orbitals (or other local functions) as the basis set
- With the arrival of GGAs, DFT has begun to dominate in the field of Quantum Chemistry
- Typically, Hamiltonians are constructed, then diagonalised to obtain the full spectrum – Order(N^3)

Order(N) Schemes

- It appears intuitive that if you double the number of atoms in your system, you might expect to have to do twice as much work
- With traditional electronic structure methods, the order(N^3) scaling with system size ensures you (or your computer) must do eight times as much work!
- Researchers are trying to exploit the so-called *nearsightedness* of the density matrix to reduce the scaling with system size
- The aim is linear scaling, allowing much larger systems to be tackled
- All approaches involve additional controlable approximations, and are not yet *black box*

The Future of Electronic Structure Methods

- More efficient, better scaling codes
  - linear scaling techniques
  - mixed methods
- Mature, reliable, easy to use codes
  - freely available (GNU license), with community support
  - commercially available, with professional support
- Improved functionals, and beyond DFT
  - Quantum Monte Carlo methods
  - GW (perturbation theory) based methods
  - feed back to new functionals
- Calculation of properties
  - linear response methods (phonons, thermodynamic quantities)
  - spectroscopic properties (e.g. optical, IR Raman, NMR, EPR)