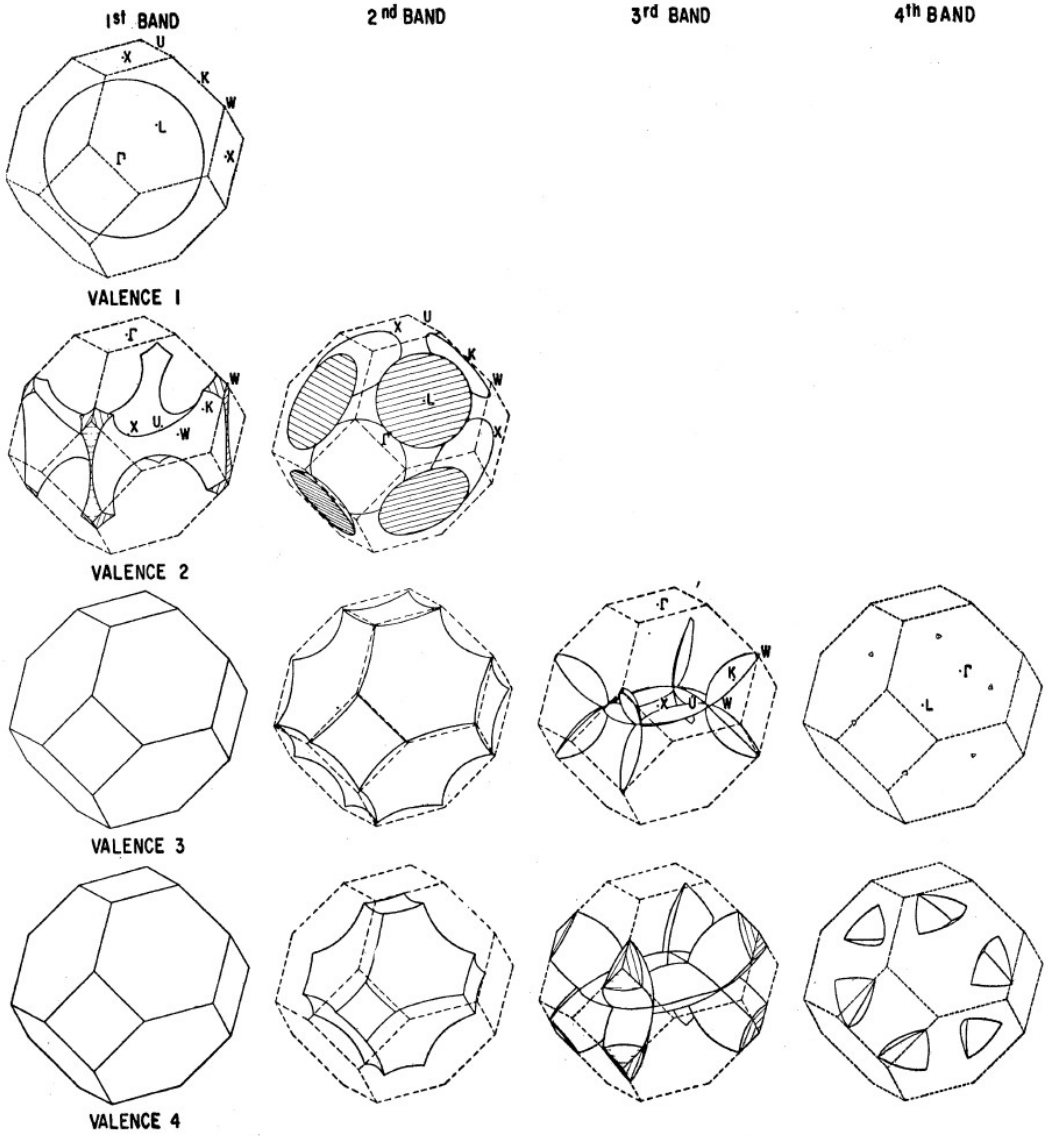
4. Electrons

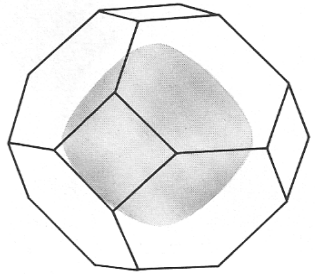
Oct 11, 2018

Fermi surface for fcc in the empty lattice approximation

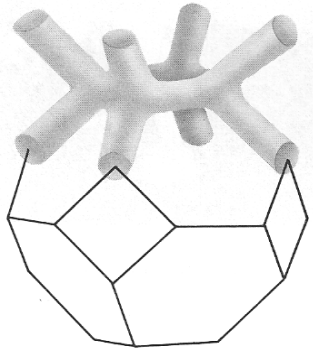


Valence 4

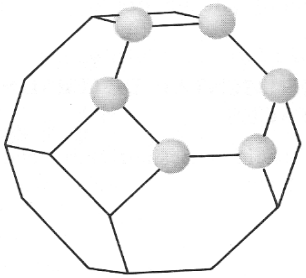
2nd zone holes



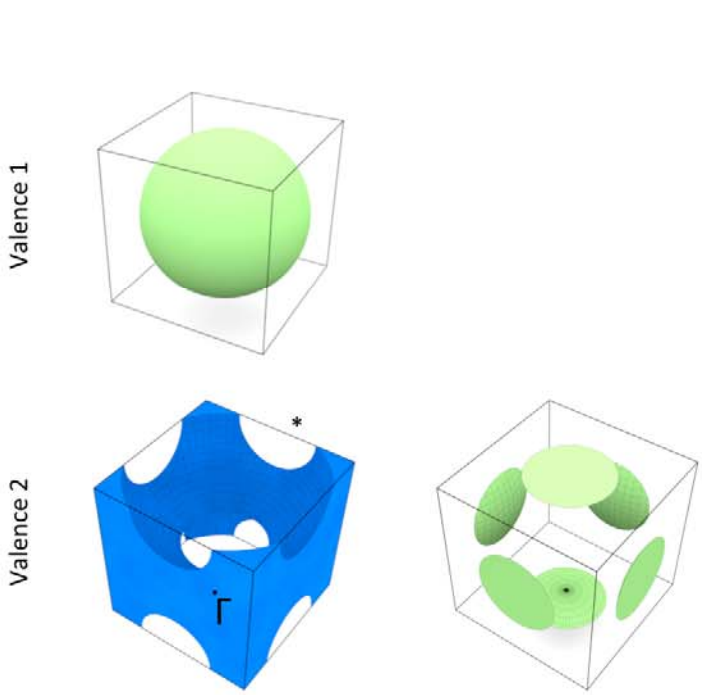
3rd zone monster

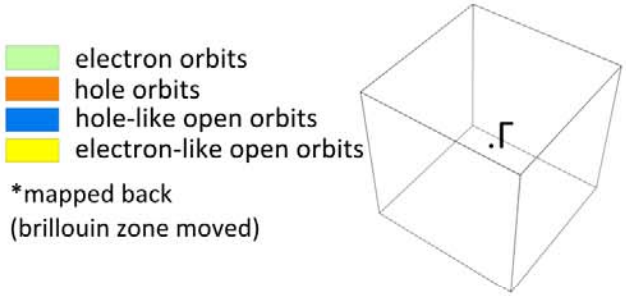


4th zone electrons



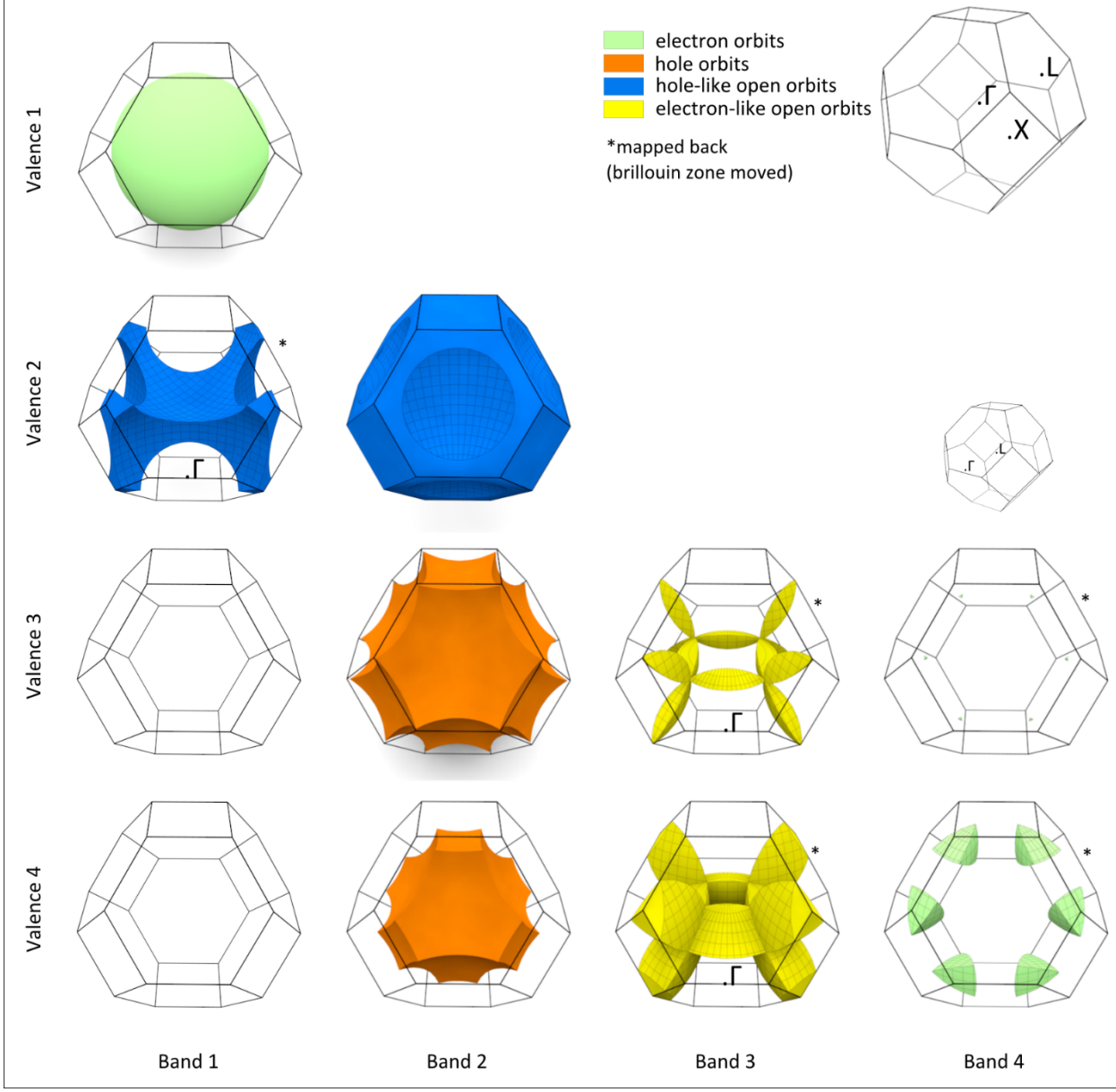
SC - Fermi surfaces in the empty lattice approximation





The flat planes are edges of the Brillouin zone boundary, not the Fermi surface.

FCC - Fermi surfaces in the empty lattice approximation



Band structure calculations

Start with the full Hamiltonian.

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_A \frac{\hbar^2}{2m_A}\nabla_A^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\varepsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 r_{AB}}$$

Everything you can know is contained in this Hamiltonian.

Usually this is too difficult to solve.

http://en.wikipedia.org/wiki/File:Erwin_Schr%C3%B6dinger.jpg

Electrons in a crystal

Fix the positions of the nuclei (Born Oppenheimer approximation) and consider the many electron Hamiltonian.

$$H_{elec} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\varepsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

This is still too difficult. Neglect the electron-electron interactions.

Separation of variables

$$H_{elec} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\varepsilon_0 r_{iA}} + \cancel{\sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}}$$

The electronic Hamiltonian separates into the molecular orbital Hamiltonians.

$$H_{\text{elec}}(r_1,r_2,\ldots r_n) = H_{\text{MO}}(r_1) + H_{\text{MO}}(r_2) + \ldots H_{\text{MO}}(r_n)$$

$$\Psi_{\text{elec}}(r_1,r_2,\ldots r_n) = |\psi_{\text{MO}}(r_1)\psi_{\text{MO}}(r_2) \ \ldots \psi_{\text{MO}}(r_n)>$$

$$H_{MO} = \frac{-\hbar^2}{2m_e}\nabla - \sum_A \frac{Z_A e^2}{4\pi\varepsilon_0 \left|\vec{r} - \vec{r}_A\right|}$$

Solving the molecular orbital Hamiltonian

$$H_{MO} = \frac{-\hbar^2}{2m_e}\nabla - \sum_A \frac{Z_A e^2}{4\pi\varepsilon_0 \left|\vec{r} - \vec{r}_A\right|}$$

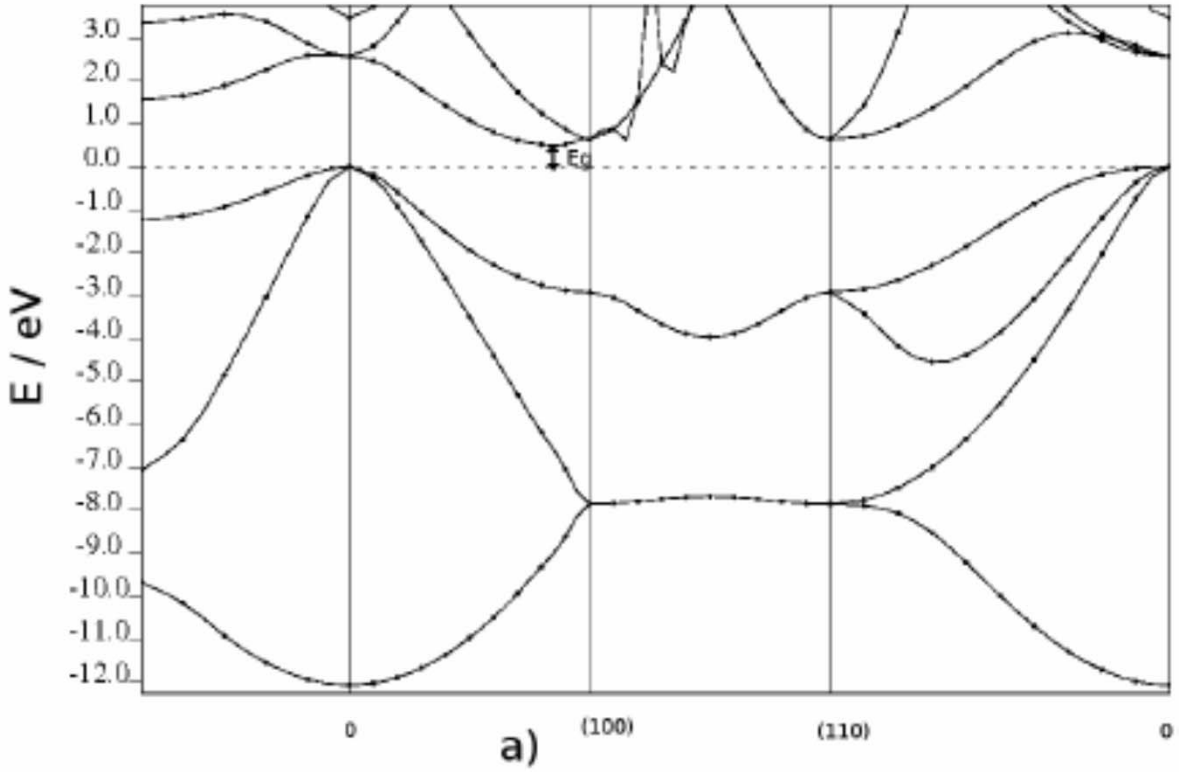
Band structure calculations:

Plane wave method
Tight binding (LCAO+)

DFT

Si

Bachelor thesis Benedikt Tschofenig



QUANTUMESPRESSO

http://www.quantum-espresso.org/

Tight binding

Tight binding does not include electron-electron interactions

$$H_{MO} = \frac{-\hbar^2}{2m_e}\nabla + V(\vec{r}) = \frac{-\hbar^2}{2m_e}\nabla - \sum_A \frac{Z_A e^2}{4\pi\varepsilon_0 \left|\vec{r} - \vec{r}_A\right|}$$

Assume a solution of the form.

$$\psi_k = \sum_{l,m,n} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3\right)\right)\sum_a c_a\phi_a\left(\vec{r} - l\vec{a}_1 - m\vec{a}_2 - n\vec{a}_3\right)$$

atomic orbitals:
choose the relevant
valence orbitals

http://lamp.tu-graz.ac.at/~hadley/ss1/bands/tightbinding/tightbinding.php

Tight binding

$$\psi_k = \sum_{l,m,n} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3\right)\right)\sum_a c_a\phi_a\left(\vec{r} - l\vec{a}_1 - m\vec{a}_2 - n\vec{a}_3\right)$$

$$H_{MO}\psi_k = E_k\psi_k$$

$$\langle\phi_a|H_{MO}|\psi_k\rangle = E_k\langle\psi_a|\psi_k\rangle$$

$$c_a\langle\phi_a|H_{MO}|\phi_a\rangle + \sum_{\text{nearest neighbors } m} c_m\langle\phi_a|H_{MO}|\phi_m\rangle\exp(i(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3)) + \text{small terms}$$

$$= E_k c_a\langle\phi_a|\phi_a\rangle + \text{small terms}$$

There is one equation for each atomic orbital

Tight binding, one atomic orbital

$$c_a \langle \phi_a | H_{MO} | \phi_a \rangle + \sum_{\text{nearest neighbors } m} c_m \langle \phi_a | H_{MO} | \phi_m \rangle \exp(i(l\vec{k} \cdot \vec{a}_1 + m\vec{k} \cdot \vec{a}_2 + n\vec{k} \cdot \vec{a}_3)) + \text{small terms}$$

$$= E_k c_a \langle \phi_a | \phi_a \rangle + \text{small terms}$$

For only one atomic orbital in the sum over valence orbitals

$$E_k c_a \langle \phi_a | \phi_a \rangle = c_a \langle \phi_a | H_{MO} | \phi_a \rangle + \sum_{\text{nearest neighbors } m} c_a \langle \phi_a | H_{MO} | \phi_m \rangle \exp(i(l\vec{k} \cdot \vec{a}_1 + m\vec{k} \cdot \vec{a}_2 + n\vec{k} \cdot \vec{a}_3))$$

one atomic orbital
$E_k = \varepsilon - t \sum_m e^{i\vec{k} \cdot \vec{\rho}_m}$

$$\varepsilon = \langle \phi_a(\vec{r}) | H_{MO} | \phi_a(\vec{r}) \rangle \qquad t = -\langle \phi_a(\vec{r}) | H_{MO} | \phi_a(\vec{r} - \vec{\rho}_m) \rangle$$