You need to compute the total density and potential in each cycle.

For each shell \( i \), you have
\[
\rho_i = 4\pi r^2
\]

and the total density \( \rho = \sum \rho_i \).

We find \( \psi_i(r) = \frac{\mu i}{r} \bar{Y} m_l(\theta, \phi) \) from
\[
\left[ -\frac{i}{2} \Delta + V + \frac{\mu^2(l+1)}{2r^2} \right] \psi_i(r) = 0
\]

For a filled shell, regardless of \( l \),
\[
\rho_i = \frac{\mu_i^2(r)}{r^2}
\]

For example, for \( l = 1 \), one can take
\[
\begin{align*}
\psi_{1r} &= \frac{x}{r} & \psi_{1\theta} &= \frac{y}{r} & \psi_{1\phi} &= \frac{z}{r} \\
\psi^2(r) &= \frac{x^2 + y^2 + z^2}{r^2} \mu_1(r) = \frac{1}{r^2} \mu_1^2(r)
\end{align*}
\]

In each case \( \mu \) can be normalized so that \( \int d^3r \frac{\mu^2(r)}{r^2} = N_e \) where \( N_e \) is the number of electrons in shell \( n, l \).

As discussed in Thijssen, you may want to keep the factor of \( \psi_i \) in \( n \) so that \( \int d^3r \mu_i = N_e \) (see 5.31).
Periodic Solids

Nuclei are at \( \vec{r}_i = \frac{2}{3} \vec{a}_i n_i + \vec{b}_i \)

\( \vec{a}_i \) = lattice vectors

\( \vec{b}_i \) = basis vectors

14 Bravais lattices

\( \vec{a}_i \) = 30 space groups

Lattice: \( \vec{R}_{ij,k} = i \vec{a}_1 + j \vec{a}_2 + k \vec{a}_3 \), \( i, j, k \) integers

Reciprocal lattice: \( \vec{G}_{h,k,l} = h \vec{g}_1 + k \vec{g}_2 + l \vec{g}_3 \), \( h, k, l \) integers.

\( R \cdot G = 2\pi n \), \( n \) integer

\( a_i \cdot g_j = 2\pi \delta_{ij} \)

\( g_j = 2\pi \) \( \epsilon_{jux} \) \( \frac{a_u \times a_v}{V} \)

\( V = a_1 \cdot (a_2 \times a_3) \)

\( \epsilon_u \epsilon_v + 1 \) even \(-1\) odd

First Brillouin zone:
All points closer to \( \vec{K} = 0 \) than to any other point \( \vec{G} \).

Van Harnan Bandgap conditions (periodic):

allowed \( K = \frac{2\pi}{L_i} \left( \frac{n_1}{L_1}, \frac{n_2}{L_2}, \frac{n_3}{L_3} \right) \)
Consider the Fourier transform of the potential

\[ V(r) = \sum_{\mathbf{G}} e^{i \mathbf{G} \cdot \mathbf{r}} V_G \]

This is a periodic potential with periodicity given by \( \mathbf{G} = h \mathbf{a}_1 + k \mathbf{a}_2 + l \mathbf{a}_3 \) constant

\( |\mathbf{G}| = 1 \) period per cell

\( \frac{1}{2} |\mathbf{G}| = 2 \) periods per cell... etc.

The orbitals (wave functions) do not have to have the periodicity of the cell.

\[ \psi(r) = \sum_{\mathbf{K}} e^{i \mathbf{K} \cdot \mathbf{r}} C_{\mathbf{K}} \]

Now \( \mathbf{K} = \mathbf{k} + \mathbf{G} \)

\( \mathbf{K} \) is not a reciprocal lattice vector.

Consider \( (-\frac{1}{2} \nabla^2 + V) \psi = \varepsilon \psi \)

\[ -\frac{1}{2} \nabla^2 \psi = \frac{1}{2} \sum_{\mathbf{K}} K^2 e^{i \mathbf{K} \cdot \mathbf{r}} C_{\mathbf{K}} \]

\[ V \psi = (\sum_{\mathbf{G}} e^{i \mathbf{G} \cdot \mathbf{r}} V_G)(\sum_{\mathbf{K}} e^{i \mathbf{K} \cdot \mathbf{r}} C_{\mathbf{K}}) \]
\[ V \psi = (\sum_k e^{iG \cdot r}) (\sum_k e^{iK \cdot r}) \]
\[ = \sum G K e^{i(K+G) \cdot r} = \sum G K e^{iK' \cdot r} \]
\[ K' = G + K \]

So Schrödinger's eq. becomes:
\[ \sum_k e^{iK' \cdot r} \left( \frac{i}{2} k'^2 - \varepsilon \right) C_k + \sum G \psi C_{K'-G} \psi = 0 \]

Now since plane waves are orthogonal, each term must be zero (can also prove by multiplying by \( G e^{iG \cdot r} \) and integrating.)

Let \( K = \vec{K} + \vec{G} \) and we set:
\[ \left( \frac{i}{2} |\vec{K} + \vec{G}|^2 - \varepsilon \right) C_{\vec{K} + \vec{G}} + \sum G \psi C_{K'-G} = 0 \]
\[ G' \rightarrow G'-G \]
\[ \left( \frac{i}{2} |\vec{K} + \vec{G}|^2 - \varepsilon \right) C_{\vec{K} + \vec{G}} + \sum G \psi C_{K'-G} = 0 \]

Note \( \vec{K} \) vectors are independent. Solve secular equation for each \( \vec{K} \), set \( \varepsilon i \vec{K} \), \( C_{\vec{K} + \vec{G}} \)

Bloch's theorem: \( \psi(r) = \sum G e^{i(K+G) \cdot r} \)
Band Theory cont'd

Bloch's Theorem:

\[
\psi_k(r) = \sum_{\mathbf{G}} C_{\mathbf{k},\mathbf{G}} e^{i(\mathbf{k} \cdot \mathbf{r} - \mathbf{G} \cdot r)}
\]

\[
\psi_k(r) = e^{i\frac{2\pi}{a}r} \left( \sum_{\mathbf{G}} C_{\mathbf{k},\mathbf{G}} e^{-i\mathbf{G} \cdot r} \right)
\]

This is a periodic function of \( r \).

\[
\psi_k(r) = e^{i\frac{2\pi}{a}r} \psi(r)
\]

Summary: assumption of band theory periodic external potential.

To solve: could form \( H_{GG} \) and diagonalize, but need too many \( G \)'s (~1 million for H1) for full potential.
Tight-Binding

Consider basis functions:
\[ \phi_{jk} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i \mathbf{k} \cdot \mathbf{r}} \phi_i (\mathbf{r} - \mathbf{R}) \]

Periodic

\[ \phi_k = \sum_i C_i (k) \phi_{ij} \]

\[ H_{jk} = \sum_{\mathbf{k}} \phi_{jk} (H) \phi_{jk} \]

Self-consistent with atomic or local basis \( \rightarrow \) LCAO
Linear Combination of Atomic Orbitals

Non-self consistent, unknown local basis \( \rightarrow \) tight binding

Tight-binding: parametrize \( H_{jk} \) and \( S_{jk} \) and diagonalize once!

\( H_{jk} \) and \( S_{jk} \) -- non-orthogonal

\( H_{jk} \) -- orthogonal

2-center:
\[ H_{jk} = \langle \phi (R_i) | H (R_j) | \phi (R_j) \rangle \]

Maintain 3 centers:
\[ H_{jk}^{13} = \frac{1}{R_{2}} \langle \phi (R_i) | H (R_j) | \phi (R_3) \rangle \]