

Orthogonalized plane wave method

- In 1D, we discussed expanding in a basis of plane waves
- 3D generalization is straight forward!

$$H = \frac{\vec{p}^2}{2m} + \sum_{\vec{t}_n \in \vec{v}} V_r (\vec{r} - \vec{d}_r - \vec{t}_n)$$

↑ lattice vectors
 ↓ basis vectors if composite lattice

* Basis functions: $w_{\vec{k}_i}(\vec{r}) = \frac{1}{\sqrt{N\Omega}} e^{i(\vec{k} + \vec{h}_i) \cdot \vec{r}}$

↑ reciprocal lattice vector
 Ω crystal volume

* Matrix elements:

$$\langle w_{\vec{k}_i} | H | w_{\vec{k}_j} \rangle = \frac{\hbar^2 k_i^2}{2m} \delta_{ij} + \frac{1}{N\Omega} \sum_{\vec{t}_n \in \vec{v}} \int e^{-i(\vec{k} + \vec{h}_i) \cdot \vec{r}} V_r (\vec{r} - \vec{d}_r - \vec{t}_n) e^{i(\vec{k} + \vec{h}_j) \cdot \vec{r}} d\vec{r}$$

- Can write: $V_r (\vec{r} - \vec{d}_r - \vec{t}_n) = \sum_{\vec{g}_m} \tilde{V}_r (\vec{g}_m) \exp[i\vec{g}_m \cdot (\vec{r} - \vec{d}_r - \vec{t}_n)]$

$$= \sum_{\vec{g}_m} \tilde{V}_r (\vec{g}_m) e^{i\vec{g}_m \cdot \vec{r}} e^{-i\vec{g}_m \cdot \vec{d}_r}$$

So matrix elements are:

$$= \frac{\hbar^2 k_i^2}{2m} \delta_{ij} + \frac{1}{N\Omega} \sum_{\vec{g}_m} \left\{ \exp[i(\vec{h}_i - \vec{h}_j + \vec{g}_m) \cdot \vec{r}] \tilde{V}_r (\vec{g}_m) d\vec{r} e^{-i\vec{g}_m \cdot \vec{d}_r} \right\}$$

$$= \frac{\hbar^2 k_i^2}{2m} \delta_{ij} + \sum_{\vec{g}_m} e^{-i(\vec{h}_i - \vec{h}_j) \cdot \vec{d}_r} \tilde{V}_r (\vec{h}_i - \vec{h}_j)$$

"Structure factor,"
depends on basis

"Form factor" just Fourier transform of \tilde{V}_r

* expand crystal wavefunction at \vec{k} :

$$\Psi_{\vec{k}}(\vec{r}) = \sum_i c_i \psi_{\vec{k}}(r)$$

* Solve secular equation:

$$\det \left| \left(\frac{k_i^2 \hbar^2}{2m} - E \right) \delta_{ij} + \sum_{\vec{j}} e^{-i(\vec{h}_i - \vec{h}_j) \cdot \vec{d}_{ij}} \tilde{\psi}_{\vec{j}}(\vec{h}_i - \vec{h}_j) \right| = 0$$

- But there is a problem with this method:
Treatment of core states requires way too many plane waves!!

* Why? Core states are very localized.

* Consider 1s state of Si:

Bohr radius
↓

• FCC lattice (w/ basis) with $a = 10.26 a_B$ (convention cell)

⇒ primitive cell volume is $\Omega = a^3/4$

• radius of 1s approx. $a_{1s} \approx a_B/Z$ ← nuclear charge

• If we want the maximum \vec{k} plane wave in our basis to have a wavelength of a_{1s} ,

$$|\vec{k}_{\max}| \approx \frac{2\pi}{a_{1s}} = \frac{2\pi Z}{a_B}$$

• Number of reciprocal lattice vectors N in sphere of radius $|\vec{k}_{\max}|$ is

$$\frac{4}{3}\pi |\vec{k}_{\max}|^3 = \frac{4}{3}\pi \frac{(2\pi)^3 Z^3}{a_B^3} = N \Omega_k = \frac{N (2\pi)^3}{\Omega} = \frac{N (2\pi)^3 4}{a^3}$$

$$N = \frac{\pi}{3} 14^3 \left(\frac{a}{a_B}\right)^3 = \frac{\pi}{3} 14^3 \cdot 10.26^3 \approx 3 \times 10^6$$

• Thus we need to solve $10^6 \times 10^6$ secular matrix to have a basis that describes Si 1s orbital

- How can we avoid this issue? In any case, we are most interested in properties of valence electrons, not core.

* Solution:

- Assume we know the form of the core states, i.e., they remain atomic-like (tight-binding picture)
- Obtain a new basis that is orthogonalized WRT the core orbitals

* Orthogonalization:

- Assume we know the first n_c eigenfunctions of H :

$$H \Psi_c = E_c \Psi_c, \quad c = 1, 2, \dots, n_c$$

- For any basis state Φ_i , consider an orthogonalized version $\tilde{\Phi}_i$:

$$|\tilde{\Phi}_i\rangle = |\Phi_i\rangle - \sum_c |\Psi_c\rangle \langle \Psi_c | \Phi_i \rangle$$

- Then we can expand any state "above" n_c as

$$|\Psi_i\rangle = \sum_j c_{ij} |\tilde{\Phi}_j\rangle, \quad i \neq 1, 2, \dots, n_c$$

- Thus to get Ψ_i 's and E_i 's, solve secular equation:

$$\det |\langle \tilde{\Phi}_i | H | \tilde{\Phi}_j \rangle - E \langle \tilde{\Phi}_i | \tilde{\Phi}_j \rangle| = 0$$

\sim not orthogonal !!

$$\Rightarrow \det |\langle \tilde{\Phi}_i | H - E | \tilde{\Phi}_j \rangle| = 0$$

$$\begin{aligned} \langle \tilde{\Phi}_i | H - E | \tilde{\Phi}_j \rangle &= \langle \Phi_i | H - E | \Phi_j \rangle - \langle \Phi_i | H - E \left[\sum_c |\Psi_c\rangle \langle \Psi_c | \Phi_j \rangle \right] \\ &\quad - \left[\sum_c \langle \Phi_i | \Psi_c \rangle \langle \Psi_c | \right] H - E | \Phi_j \rangle \\ &\quad + \sum_{cc'} \langle \Phi_i | \Psi_c \rangle \langle \Psi_c | H - E | \Psi_{c'} \rangle \langle \Psi_{c'} | \Phi_j \rangle \end{aligned}$$

$$\begin{aligned}
&= \langle \Phi_i | H - E | \Phi_j \rangle - \langle \Phi_i | \left[\sum_c (E_c - E) | \Psi_c \rangle \langle \Psi_c | \right] | \Phi_j \rangle \\
&\quad - \langle \Phi_i | \left[\sum_c (E_c - E) | \Psi_c \rangle \langle \Psi_c | \right] | \Phi_j \rangle \quad \text{cancels one of prev. terms} \\
&\quad + \langle \Phi_i | \left[\sum_{cc'} (E_c - E) | \Psi_c \rangle \langle \Psi_c | \Psi_{c'} \rangle \langle \Psi_{c'} | \right] | \Phi_j \rangle
\end{aligned}$$

$$= \langle \Phi_i | \left[H - E + \underbrace{\sum_c (E - E_c) | \Psi_c \rangle \langle \Psi_c |}_{V^{\text{rep}}} \right] | \Phi_j \rangle$$

- So we can write the secular equation in terms of original basis functions:

$$\det | \langle \Phi_i | H + V^{\text{rep}} | \Phi_j \rangle - E \delta_{ij} | = 0$$

- Note that eigenvalues of \uparrow gives coeff of $|\Psi_i\rangle = \sum_j c_{ij} |\hat{\Phi}_j\rangle$
- V^{rep} for $E > E_c$ is a repulsive potential, increases energy above core states
- Note V^{rep} is a nonlocal potential! I.e., in position basis:

$$\langle r | V^{\text{rep}} | r' \rangle = \sum_c (E - E_c) \Psi(r) \Psi(r') = V^{\text{rep}}(r, r') \neq V^{\text{rep}}(r) \delta(r - r')$$

* Description of core and valence states see discussion
on tight binding

- Core \rightarrow Bloch sums of atomic orbitals $\Phi_E^c(\vec{r})$
- Valence \rightarrow Orthogonalized plane waves:

$$|\tilde{W}_{\vec{k}_j}\rangle = |W_{\vec{k}_j}\rangle - \sum_{\text{core}} |\Phi_E^c\rangle \langle \Phi_E^c| W_{\vec{k}_j}\rangle$$

plane wave w/ $\vec{k}_j = \vec{k} + \vec{h}_j$

- Secular equation: $\det | \langle \tilde{w}_{\vec{k}_i} | H | \tilde{w}_{\vec{k}_j} \rangle - E \langle w_{\vec{k}_i} | w_{\vec{k}_j} \rangle | = 0$
- Or alternatively:

$$\det | \langle w_{\vec{k}_i} | \underbrace{\frac{\vec{p}^2}{2m} + V}_{\text{Crystal H}} + V^{\text{rep}} | w_{\vec{k}_j} \rangle - E \delta_{ij} | = 0$$

$$V^{\text{rep}} = \sum_{\text{core}} (E - E_c) |\Phi_{\vec{R}}^c\rangle \langle \Phi_{\vec{R}}^c|$$
- So to compute the matrix elements, we need overlaps between Φ^c and $w_{\vec{k}_i}$:

$$\begin{aligned} \langle \Phi_{\vec{R}}^c | w_{\vec{k}_i} \rangle &= \int \langle \Phi_{\vec{R}}^c | \vec{r} \rangle \langle \vec{r} | w_{\vec{k}_i} \rangle d^3 r \\ &= \frac{1}{\sqrt{N}} \sum_{\vec{t}_n} \left\{ e^{-i\vec{k} \cdot \vec{t}_n} \Phi_c^*(\vec{r} - \vec{t}_n) \cdot \frac{1}{\sqrt{N\Omega}} e^{i(\vec{k} + \vec{h}_i) \cdot \vec{r}} d^3 r \right. \\ &= \frac{1}{N\sqrt{\Omega}} \sum_{\vec{t}_n} \int e^{i(\vec{k} + \vec{h}_i) \cdot (\vec{r} - \vec{t}_n)} \Phi_c^*(\vec{r} - \vec{t}_n) d^3 r \\ &\quad \text{at each } \vec{t}_n, \text{ change variables to get same term as } \vec{t}_n = 0 \\ &= \frac{1}{\sqrt{\Omega}} \int e^{i(\vec{k} + \vec{h}_i) \cdot \vec{r}} \Phi_c^*(\vec{r}) d^3 r \end{aligned}$$

- Core atomic-like orbital can be written as a radial part times spherical harmonic:

$$\Phi_c(\vec{r}) = R_{nl}(r) Y_{lm}(\vec{\theta}) \quad (\text{for } n, l, m \text{ quantum numbers})$$

- Can also write plane wave in terms of spherical harmonics:

$$e^{i\vec{k}_i \cdot \vec{r}} = 4\pi \sum_{lm} i^l j_l(k_i r) Y_{lm}^*(\vec{k}_i) Y_{lm}(\vec{r})$$

spherical Bessel function
order l
magnitude of k_i

$$Y_{lm}(\vec{z}) = Y_{lm}(\theta_2, \phi_2)$$

- Then we have:

$$\begin{aligned}
 & \left\langle \Phi_{\vec{k}}^{nem} | W_{\vec{k}_i} \right\rangle = \frac{4\pi}{\sqrt{\omega}} \sum_{\ell m} \int i^{\ell'} j_{\ell'}(k_i r) Y_{\ell'm'}^*(\vec{k}_i) Y_{\ell'm'}(\vec{r}) R_{ne}(r) Y_{\ell'm'}^*(\vec{r}) dr \\
 &= \frac{4\pi}{\sqrt{\omega}} \sum_{\ell m} Y_{\ell'm'}^*(\vec{k}_i) i^{\ell'} \underbrace{\int \int Y_{\ell'm'}(\vec{r}) Y_{\ell'm'}^*(\vec{r}) \sin \theta d\phi d\theta}_{\delta_{\ell\ell'} \delta_{mm'}} \int j_{\ell'}(k_i r) R_{ne}(r) r^2 dr \\
 &= \frac{4\pi}{\sqrt{\omega}} Y_{\ell'm'}^*(\vec{k}_i) i^{\ell'} \int j_{\ell'}(k_i r) R_{ne}(r) r^2 dr
 \end{aligned}$$

- So:

$$\begin{aligned}
 \left\langle W_{\vec{k}_i} | V^{rep} | W_{\vec{k}_j} \right\rangle &= \sum_{nem}^{\text{core}} (E - E_{ne}) \left\langle W_{\vec{k}_i} | \Phi_{\vec{k}}^{nem} \right\rangle \left\langle \Phi_{\vec{k}}^{nem} | W_{\vec{k}_j} \right\rangle \\
 &= \sum_{ne}^{\text{core}} (E - E_{ne}) P_L(\hat{k}_i \cdot \hat{k}_j) A_{ne}(|k_i|) A_{ne}(|k_j|) \\
 \text{Legendre polynomial: } P_L(\hat{k}_i \cdot \hat{k}_j) &= \sum_{m=-L}^{+L} Y_{\ell'm}^*(\vec{k}_i) Y_{\ell'm}(\vec{k}_j) \\
 A_{ne}(|k_i|) &= i^{\ell} \sqrt{\frac{4\pi(2\ell+1)}{\omega}} \int_0^{\infty} R_{ne}(r) j_{\ell}(k_i r) r^2 dr
 \end{aligned}$$

- Many other methods (see G and P Ch. V) have similar spirit of combining plane waves for itinerant valence / conduction electrons with radial / atomic functions for core states

Pseudopotential method

- OPW allows us to separate "inert" core from valence states (or unoccupied "conduction" states)
- **Problem:** we still have to deal with the full crystal potential $V(r)$
 - * Atomic-like so strong in the core region
 - * Also, valence-electron wavefunctions will have oscillations in core region since they need to be orthogonal to core
- **Solution:** replace crystal potential in core region with a weaker "pseudopotential"
 - * Eigenstates will be "pseudo wavefunctions," only required to match true wavefunctions outside of core region
 - * We kind of did this w/ OPW, V^{rep} cancels some of $V(\vec{r})$ in the core region
 - * replace $V + V^{\text{rep}}$ with V^{psp} :
$$\det \left| \left(\frac{\hbar^2 k_i^2}{2m} - E \right) \delta_{ij} + \sum_{\vec{r}} e^{-i(\vec{k}_i - \vec{k}_j) \cdot \vec{r}} V_r^{\text{psp}} (\vec{k}_i - \vec{k}_j) \right| = 0$$
 - * Can often choose V^{psp} to have few Fourier components
 - Example in G and P Sec. U.4 (and HW 5): band structure of Si with just three parameters and ~ 40 reciprocal lattice vectors

- How do we determine V^{PSP} ?

* Empirical pseudopotentials: fit to experiment or other calculations (Si example)

* Atomic/ab-initio pseudopotentials: Calculate V of free atom, take exact V outside of radius r_c from core, use approximate (weak) form inside of r_c

- Simplest form: $V^{\text{PSP}}(r) = \begin{cases} A & \text{for } r < r_c \\ -\frac{e^2}{r} & \text{for } r > r_c \end{cases}$

- Another prescription: Parametrize radial pseudowavefunctions as:

$$R^{\text{PSP}}(r) = \begin{cases} r^l e^{p(r)} & \text{for } r < r_c \\ R_a(r) & \text{for } r > r_c \end{cases}$$

adjustable parameters

where $p(r) = \lambda_0 + \lambda_2 r^2 + \lambda_3 r^3 + \lambda_4 r^4$

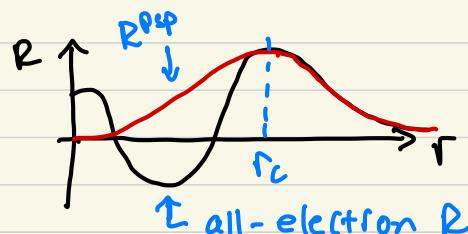
plug into radial S.E. to get:

$$V^{\text{PSP}}(r) = \begin{cases} E_a + \frac{2(l+1)}{r} p'(r) + p''(r) + [p'(r)]^2 & \text{for } r < r_c \\ V_a(r) & \text{for } r > r_c \end{cases}$$

energy of atomic radial wavefunction
no linear term in p
so $p'(r) \propto r$ as $r \rightarrow 0$

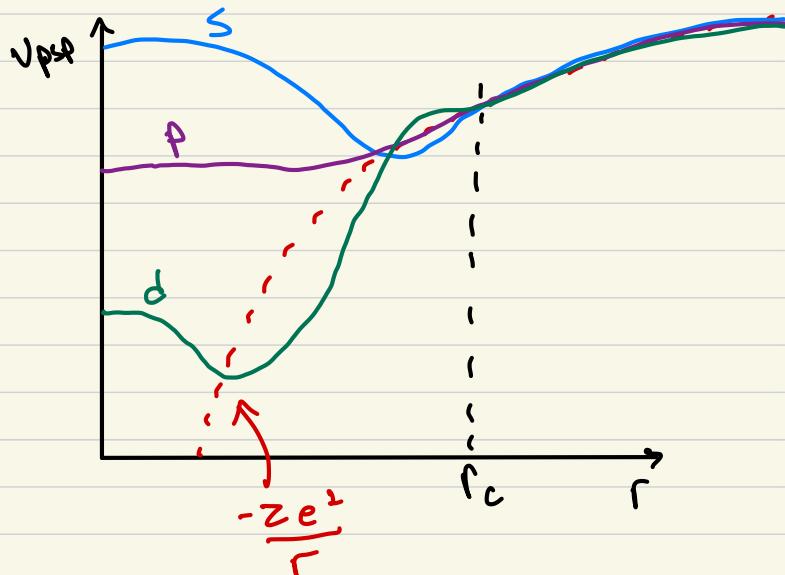
- Choose λ 's so wavefunction is normalized to 1 to conserve charge in core region, and $R(r_c)$ and derivatives are continuous

- Note: R^{PSP} has no nodes:



- Note: V^{PSP} is different for different angular momentum. In practice, it will have a nonlocal part of the form

$$V_{NL}^{PSP} = \sum_{nem} |\Phi_{nem}\rangle \langle \Phi_{nem}|$$



- Most popular modern "ab initio" treatment of solids use plane waves and pseudo potentials!

Methods for describing bands in 3D What have we learned?

- Can describe bands in 3D empirically with relatively few free parameters
- Tight - binding: Make Bloch sums for different types of orbitals, parametrize matrix elements based on orbital type and direction
 - * Often most convenient for (semi) analytical description of solids
- Plane - wave expansion: Have to combine localized atomic - like functions for core electrons with itinerant plane waves
 - + Often most convenient for full numerical treatment of solids