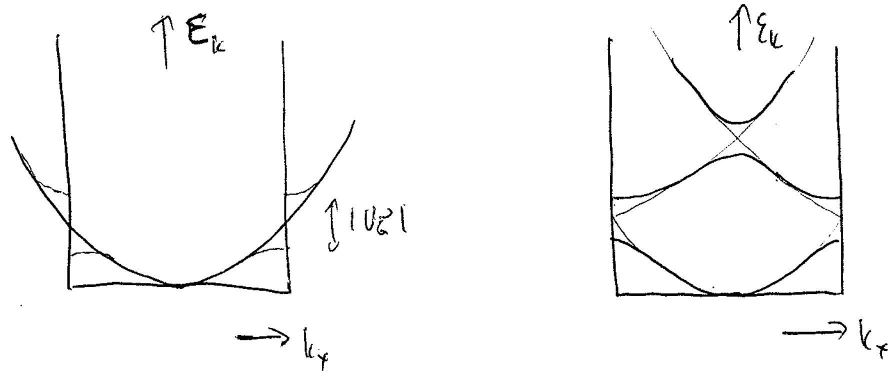
* We've looked at band structure from two simple extremes:

① free-electron plane waves weakly perturbed by the periodic potential

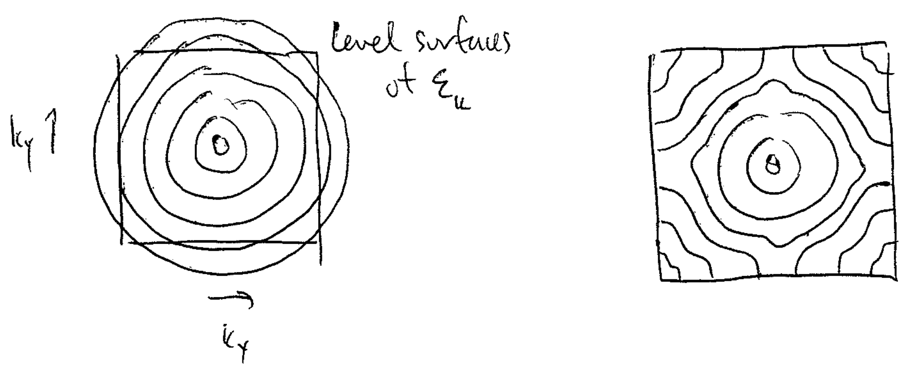
→ back-folding of parabolic dispersion into the BZ

→ gap opens due to Bragg scattering along the plane $\vec{k} = \frac{1}{2}|\vec{G}|$ with strength $U_{\vec{G}}$

1D



2D

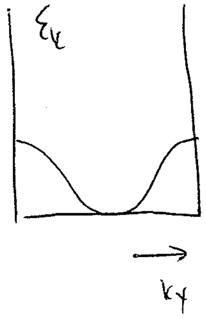


② tight-binding expansion in terms of localized atomic orbitals

→ compute hopping matrix elements and overlaps truncated in neighbour range

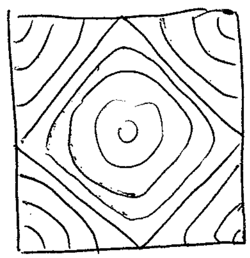
→ solve generalized eigenvalue problem made block diagonal in $\vec{k}$

1D



$2t\,(1-\cos k_x a)$

2D



level surfaces of $-2t\,(\cos k_x a + \cos k_y a)$

→ only as many bands as atomic orbitals we choose to include:

$$\psi_{\vec{k},n} = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \sum_{\vec{\tau},\alpha} C^{(n)}_{\vec{\tau},\alpha}\, \phi_\alpha(\vec{r}-\vec{R}-\vec{\tau})$$

wave vector band index basis elements orbital type

n ranges from 1 to #basis × #orbitals

* Differently adapted:

nearly-free-electron		tight-binding
extended w.f.		localized
wide band		narrow band
metallic		insulating
hard to achieve fast oscillations in the core	← technical issues →	hard to work with nonorthogonal wavefunctions

Wannier functions

* An alternative basis of localized functions

→ construct as Fourier transform of any set of Bloch wave functions

$$w_n(\vec{r}-\vec{R}) = \sum_k e^{-i\vec{k}\cdot\vec{R}} \psi_{nk}(\vec{r})$$

→ orthonormal so long as the Bloch set is

$$\int d^3r\, w_{n'}^*(r-R')\, \phi_n(r-\vec{R}) = \int d^3r \sum_{k,k'} e^{-ik\cdot R+ik'\cdot R'} \psi_{n'k'}(\vec{r})\, \psi_{nk}(\vec{r})$$

$$= \sum_{kk'} e^{-ik\cdot R+ik'\cdot R'} \underbrace{\int d^3 \psi_{n'k'}(\vec{r}) \psi_{nk}(\vec{r})}_{\delta_{nn'}\delta_{kk'}}$$

$$= \sum_k e^{-ik\cdot(R-R')} \delta_{nn'}$$

$$= \delta_{R,R'}\delta_{n,n'}$$

→ additional phase freedom to define

$$\tilde{w}_n(\vec{r}-\vec{R}) = \sum_k e^{-i\vec{k}\cdot\vec{R}+i\phi(\vec{k})} \psi_{n\vec{k}}(\vec{r})$$

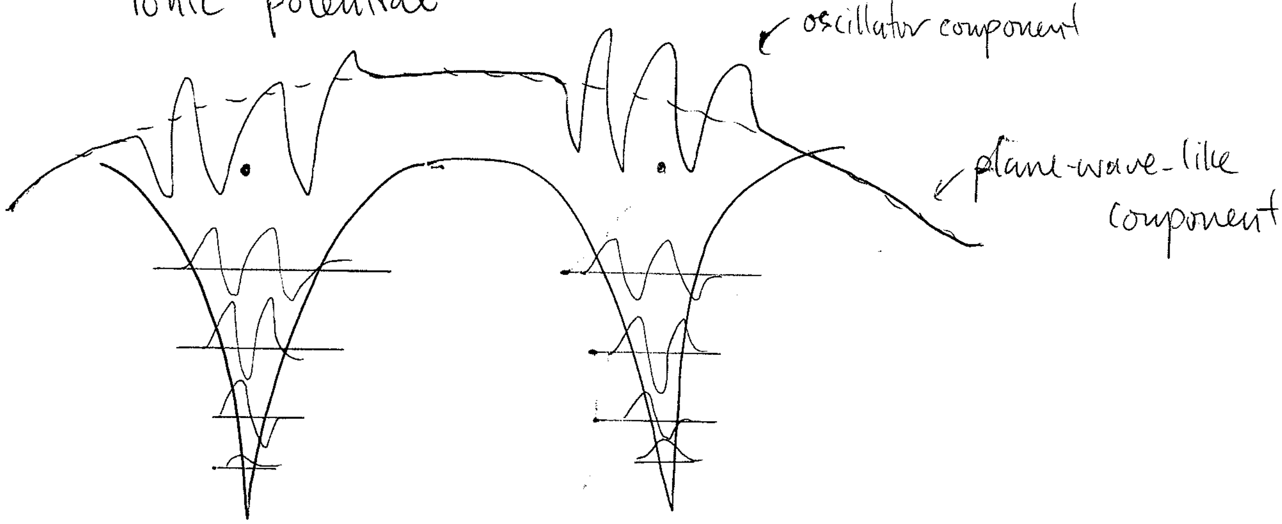
arbitrary real function

→ optimize $\tilde{w}_n$ by choosing $\phi(\vec{k})$ so that $\tilde{w}_n$ falls off quickly in $|\vec{r}-\vec{R}|$

Orthogonalized Plane-wave (OPW)

* nearly-free electron model does not account for the rapid oscillator region in the core region of the ions

* tight-binding does a good job in the core but not in the interstitial regions where there are strong contributions from the continuum of states above the ionic potential



* OPW method
  → start with complete set of Bloch w.f.s for the core states

$$\phi_{c\vec{k}}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi_c(\vec{r}-\vec{R})$$

  → let $\chi_k(\vec{r})$ be a higher energy state that is plane-wave-like but orthogonal in the core

$$\chi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} - \sum_c \alpha_c \phi_{c\vec{k}}(\vec{r})$$

→ impose $0 = \int d^3r\, \phi^*_{ck}(r)\, \chi_k(\vec{r})$

$$= \int d^3r\, \phi^*_{ck}(r)\, e^{i\vec{k}\cdot\vec{r}} - \sum_{c'} \alpha_{c'} \underbrace{\int d^3r\, \phi^*_{ck}(\vec{r})\, \phi_{c'k}(\vec{r})}_{\delta_{cc'}}$$

$$= \int d^3r\, \phi^*_{ck}(r)\, e^{ik\cdot r} - \alpha_c$$

orthogonal (known) core states

- e.g. if the core states are 2s, 2p orbitals, $\chi_k(\vec{r})$ will behave like a 3s or 3p with an extra nodal surface.

→ ~~create~~ replace linear combinations

$$\psi_k(\vec{r}) = \sum_{\vec{G}} C_{\vec{G}}\, e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \rightarrow \sum_{\vec{G}} C_{\vec{G}}\, \chi_{k+G}(\vec{r})$$

→ in practice, sum is up to some cutoff in $|\vec{G}|$

→ find set of $\{C_{\vec{G}}\}$ values that minimizes the energy expectation value

$$E = \frac{\int d^3r\, \psi_k(r)^*\, H\, \psi_k(r)}{\int d^3r\, |\psi_k(r)|^2}$$

Pseudopotentials

* trick to replace the one-body potential $V(r)$ with a nonlocal one that is solved self consistently

→ assume $\psi_k(\vec{r}) = \sum_{\vec{G}} c_{\vec{G}} \chi_{k+G}(\vec{r})$ (OPW)

with c_G determined variationally is an exact crystal eigenstate

→ construct $\phi_k(\vec{r}) = \sum_{\vec{G}} c_G e^{i(k+\vec{G})\cdot\vec{r}}$ with same coeffs

→ since $\psi_k(r)$ is orthogonal to the core states, $\hat{1} - \sum_c |\phi_{ck}\rangle\langle\phi_{ck}|$

$$\psi_k(\vec{r}) = \phi_k(r) - \sum_c \langle \phi_{ck} | \phi_k \rangle \phi_{ck}(r)$$

→ TISE $H\psi_k(\vec{r}) = \varepsilon_k \psi_k(r)$

under substitution of the above is

$$H\phi_k - \sum_c \langle\phi_{ck}|\phi_k\rangle \underbrace{H\phi_{ck}(r)}_{= \varepsilon_{ck}(r)\phi_{ck}(r)} = \varepsilon_k \phi_k(r) - \varepsilon_k \sum_c \langle\phi_{ck}|\phi_k\rangle \phi_{ck}(r)$$

→ $$H\phi_k + \underbrace{\sum_c (\varepsilon_k - \varepsilon_{ck}) \langle\phi_{ck}|\phi_k\rangle \phi_{ck}(r)}_{\text{treat as repulsive } V_R \cdot \phi_k(r)} = \varepsilon_k \phi_k(r)$$

* Now have an effective Hamiltonian $H + V_R$

→ satisfies $(H+V_R)\phi_k = \varepsilon_k \phi_k$

→ self-consistency condition

$$V_R \phi_k(r) \equiv \sum_c (\varepsilon_k - \varepsilon_k) \langle \phi_{ck} | \phi_k \rangle \phi_{ck}(r)$$

$$= \int V_R(\vec{r}, \vec{r}\,') \phi_k(\vec{r}\,') \, d^3 r'$$

where $V_R(r, r') = \sum_c (\varepsilon_k - \varepsilon_{ck}) \phi_{ck}(\vec{r}) \phi_{ck}^\dagger(\vec{r}\,')$

* Hamiltonian

$$H\phi_k = -\frac{\hbar^2 \nabla^2 \phi_k}{2m} + \int \underbrace{\overbrace{\left[V(r)\delta(r-r') + V_R(r,r') \right]}^{\text{substantial cancellation}}}_{\substack{\text{pseudopotential that} \\ \text{smooths out the } \frac{1}{r} \text{ singularity} \\ \text{in the ion core}}} d^3r' \, \phi_k(r)$$

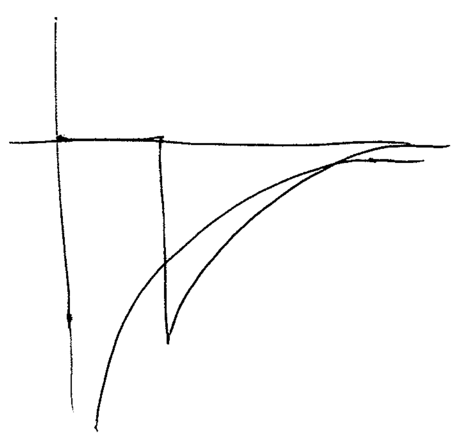
Empirical pseudopotentials

* choose (rather than calculate) a pseudopotential that matches the experimentally determined reality

→ e.g. Ashcroft potential

$$U(r) = \begin{cases} 0 & \text{if } r < R_c \quad (\text{"radius" of core}) \\ -V_0 \dfrac{e^{-r/d}}{r} & r > R_c \end{cases}$$

free parameters R_c, V_0, d can be adjusted to give a good fit for alkali metals



"First-principles" pseudopotentials

* computed within the context of DFT

Density Functional Theory

$$\hat{H}\Psi = [\hat{T} + \hat{U} + \hat{V}]\Psi = \left[\sum_{i=1}^{N}\left(-\frac{\hbar^2\nabla_i^2}{2m} + U(r_i)\right) + \sum_{i<j} V(r_i, r_j)\right]\Psi = E\Psi$$

single-particle kinetic and potential terms

many-body interaction term

→ systematic expansion in the particle density $n(\vec{r})$

$$n(\vec{r}) = N\int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \left|\Psi(\vec{r}_1, \vec{r}_2, r_3 \ldots r_N)\right|^2$$

→ In the g.s. Ψ_0, the density is $n_0 = n[\Psi_0]$.
Hohenberg and Kohn showed that this relation is invertible:

$\Psi_0 = \Psi[n_0]$ unique function of g.s. density

→ follows for any g.s. observable

$$O[n_0] = \langle\Psi[n_0]|\hat{O}|\Psi[n_0]\rangle$$

including the g.s. energy

$$E_0 = E[n_0] = \langle\Psi[n_0]|\hat{T} + \hat{U} + \hat{V}|\Psi[n_0]\rangle$$

→ view periodic potential $U[n_0]$ as $U[n] = \int U(\vec{r})\, n_0(r)\, d^3r$ evaluated at $n = n_0$ (exact)

→ assume same can be done for $T[n]$ and $V[n]$

Hence. g.s. Energy is achieved ~~at~~ for the $n = n_0$ that minimizes the functional

$$E[n] = T[n] + \int d^3r\, U(\vec{r})\, n(\vec{r}) + V[n]$$

need good approximations for these.