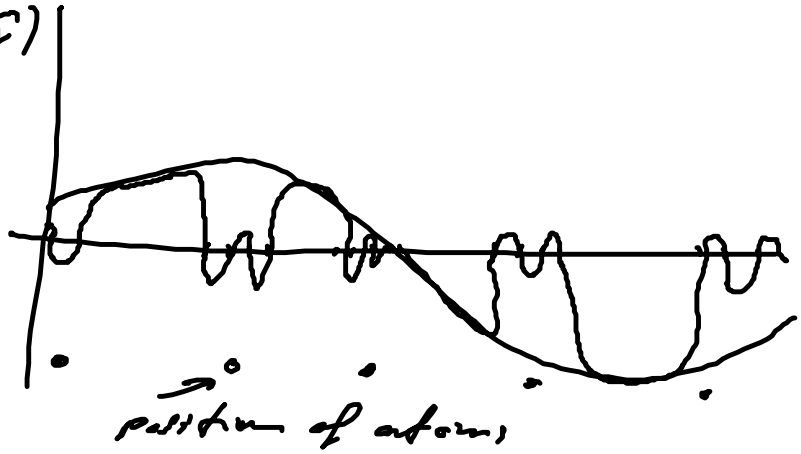
5.6 other methods for solving the Kohn Sham equation for periodic crystal

So far: nearly free electron
2) LCAO

Truth is in between



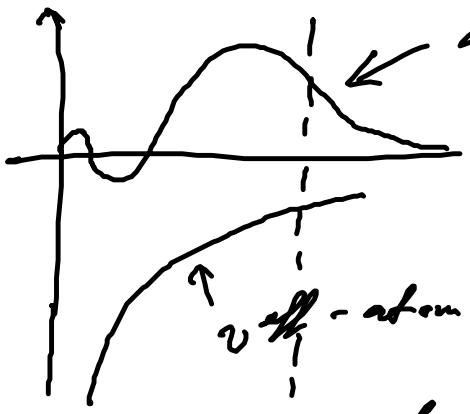
close to nuclei the wavefunction looks atomic like.

Somewhat away from nuclei it is smooth.

close to nuclei : big gradient ;
high kinetic energy

5.6 Pseudopotential method

free atom



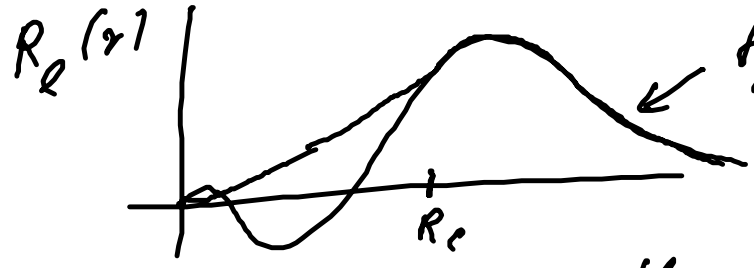
typical interatomic $\frac{1}{2}$ distance in solids

for chemical & physical properties of materials the core region is not so important

↑ extend of core state

$\Rightarrow$ replace $v^{eff-atom}$ by $v^{eff-pseudo}$

where $v^{eff-pseudo}$ has orbitals with reduced oscillations



for $r > R_c$ the true & the pseudo wavefunction must agree.

$$\int_0^{R_c} R_l^{pseudo} r^2 dr = \int_0^{R_c} R_l^{true} r^2 dr \equiv \text{norm-conservation}$$

Advantage: plane wave basis is good for describing the "pseudo" situation without loosing much accuracy.

How to do this?

1) calculate φ^{atom}
2) build φ^{pseudo} (this unique; many possibilities exist)

3) $\left(-\frac{\hbar^2}{2m}\nabla^2 + \underline{v^{eff-atom}}\right)\varphi^{atom} = \epsilon\,\varphi^{atom}$

$$\left(\frac{-\hbar^2}{2m}\nabla^2 + \underline{v^{eff-pseudo}}\right)\varphi^{pseudo} = \epsilon\,\varphi^{pseudo}$$

$$\boxed{v^{eff-pseudo} = \frac{\epsilon\,\varphi^{pseudo} - \frac{\hbar^2}{2m}\nabla^2\varphi^{pseudo}}{\varphi^{pseudo}}}$$

"inverse Schrödinger eqn."

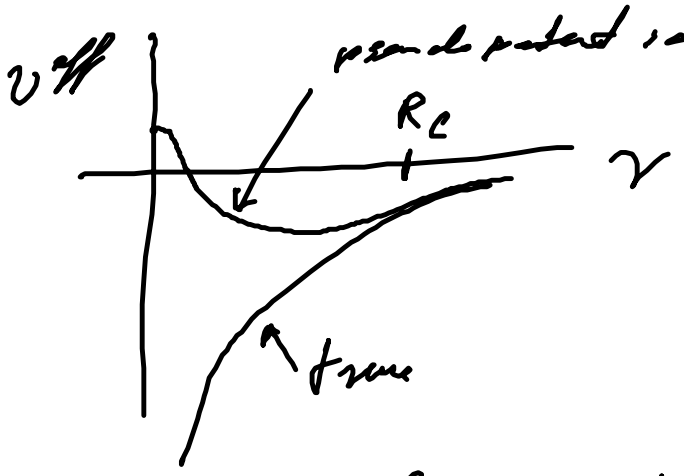
4) construct $\underline{\underline{v^{pseudo}}}$ = input for a self consistent Kohn-Sham eqn.

$$= v^{eff-pseudo} - v^{Hartree}[n^{pseudo}]$$

v^{pseudo} & $v^{eff-pseudo}$ are now ℓ-dependent

$$- v^{xc}[n^{pseudo}]$$

$$\boxed{V^{pseudo} = \sum_{\ell} v_{\ell}^{pseudo} |\ell><\ell|}$$



divergence at $r = 0$ is gone.

An expansion of hamiltonian and wavefunction in plane wave is efficient

Properties of ab initio pseudopotentials

1) for atomic calculation pseudo & true have the same eigenvalues [for valence states]
There are no core states.

2) pseudo & true wavefunction agree for $r \geq R_c$ i.e. in the chemically important region.

3) at energy $\epsilon = \epsilon_\ell$ and in the neighborhood $\epsilon = \epsilon_\ell \pm \Delta$ the scattering properties of true & pseudo potential agree.

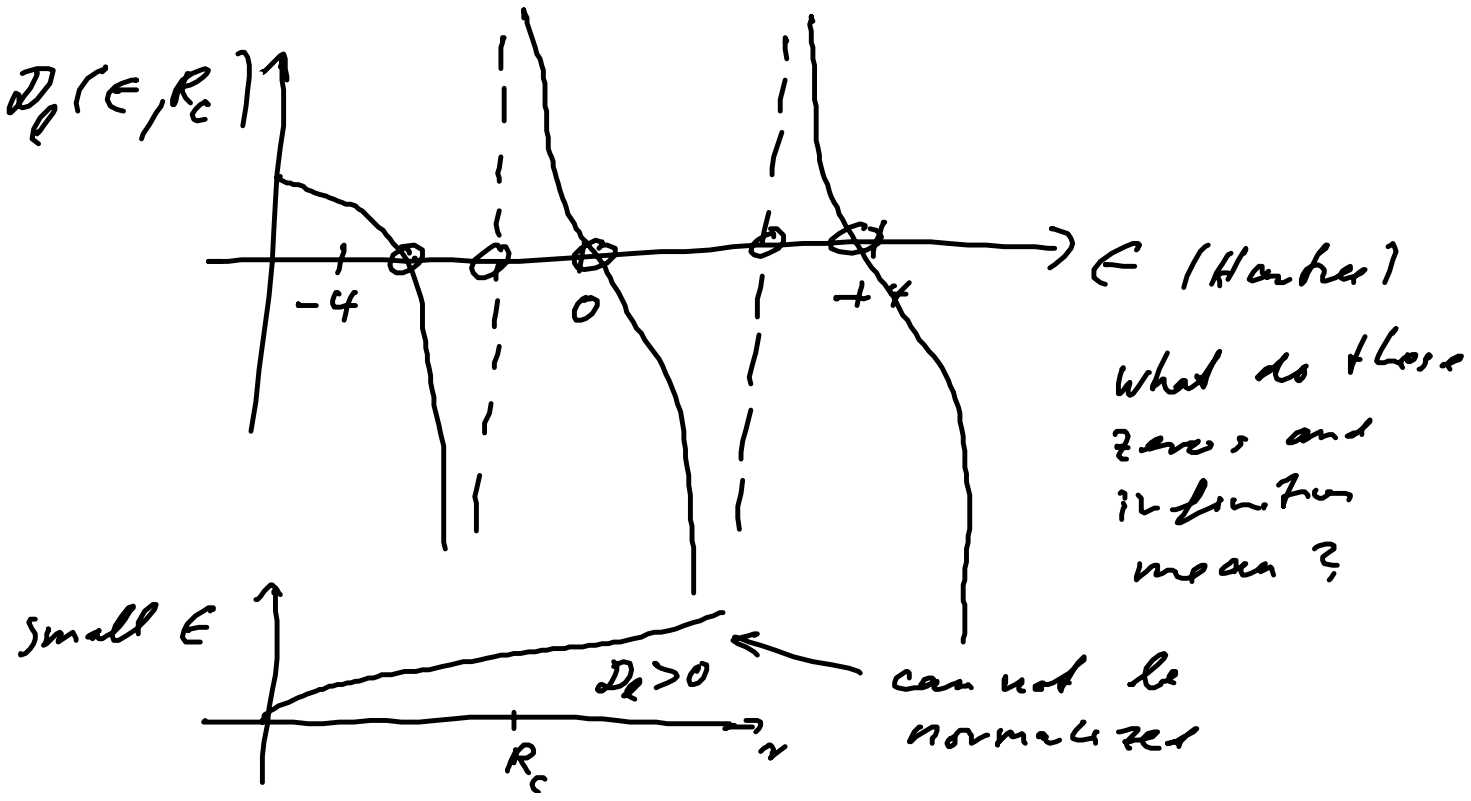
logarithmic derivative

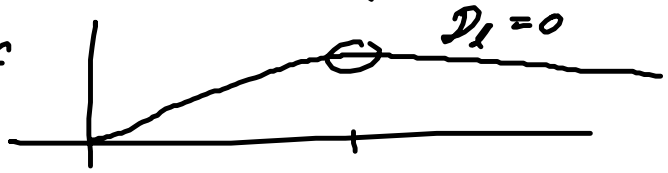
$$D_\ell(\epsilon, \underset{\text{Radius}}{\hat{R}}) \doteq \frac{1}{r} \frac{d \ln R_\ell(\epsilon, r)}{d \ln r}\Bigg|_{r=\hat{R}} = \frac{R_\ell'(\epsilon r)}{R(\epsilon, r)}\Bigg|_{r=\hat{R}}$$

R_ℓ = radial wave function

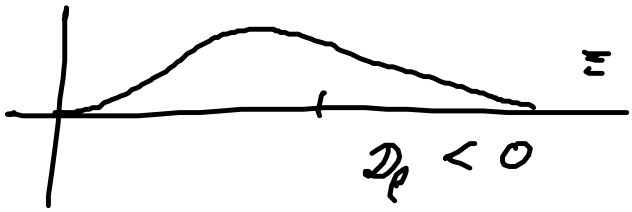
$\hat{R}$ = Radius bigger than R_c

$$\frac{d D_\ell^{\text{pseudo}}}{d\epsilon}\Bigg|_{\epsilon=\epsilon_\ell} = \frac{d D_\ell^{\text{true}}}{d\epsilon}\Bigg|_{\epsilon=\epsilon_\ell}$$

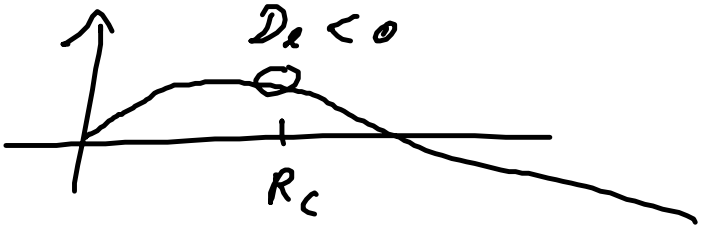


high ϵ 

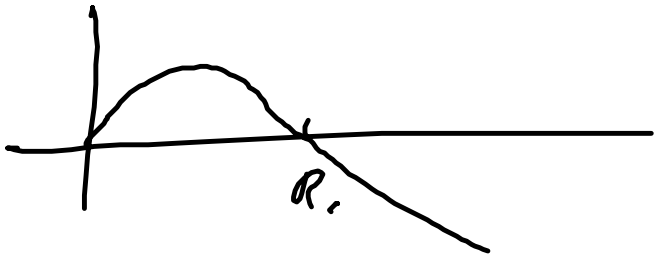
still not normalizable

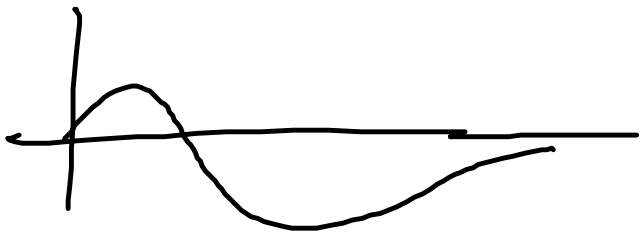
$\epsilon = \epsilon_l$ 

= eigenfunction

high ϵ 

not normalizable

high 

high 
again an eigenstate

Problem of the pseudopotential approach

1) frozen core approx.
(core states cannot adjust to new environment)

2) pseudization
for $r < R_c$ potential & wavefunctions are not correct.

3) treatment of xc between valence and core is not correct.

Typically o.k.; high pressure

5.6.2. APW and LAPW (most accurate)

augmented plane waves (Slater)
linearized augmented plane waves (O.K. Andersen)

separate space into two regions
- atomic like region (sphere $r \le R_c$)
- interstitial = space not covered by spheres.

$$v^{eff}(\vec{r}) = \begin{cases} \sum_{\ell m} v_{\ell m}^{eff}(|\vec{r}-\vec{R}_I|) Y_{\ell m}(\Omega_{\vec{r}-\vec{R}_I}) & \text{for } \vec{r} \text{ inside sphere } I \\ \sum_{\vec{G}} v^{eff}(\vec{G}) e^{i\vec{G}\vec{r}} & \text{otherwise} \end{cases}$$

This is not an approx.; just a separation into regions.

Basis set

$$\chi_{\vec{G}}^{APW}(\vec{k},\vec{r}) = \begin{cases} \sum_{\ell m} g_{\ell m}(\vec{k},\vec{G}) R_\ell(|\vec{r}-\vec{R}_I|,\epsilon) Y_{\ell m} & \text{for } \vec{r} \text{ inside sphere } I \\ \frac{1}{\sqrt{V_g}} e^{i(\vec{k}+\vec{G})\vec{r}} & \text{otherwise} \end{cases}$$

$$\frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2 = \epsilon$$

best quality basis, but very inefficient.

Basis depends on ϵ

Matrix $\langle \chi_G(\epsilon) | h | \chi_{G'}(\epsilon) \rangle$ = energy dependent

$h\varphi = \epsilon \varphi$

$\Rightarrow$ linear eigenvalue problem

$\Rightarrow$ non-linear eigenvalue problem is very hard to deal with.

LAPW

$\equiv$ replace $\sum g_{lm}(\vec{k}, \vec{G})\, R_l(|\vec{r} - \vec{R}_I|, \epsilon)\, Y_{lm}$

by $\sum_{l,m} \left[A_{lm} R_l(|\vec{r} - \vec{R}_I|, \epsilon_l^v) + B_{lm} \dot{R}_l(\vec{r} - \vec{R}_I, \epsilon_l^v) \right] Y_{lm}$

ϵ_l^v fixed energy

R_l and $\dot{R}_l = \frac{d}{d\epsilon} R_l(r, \epsilon)$ are linear independent: $\int_0^{R_c} R_l \cdot \dot{R}_l\, r^2 dr = \frac{1}{2} \frac{\partial}{\partial \epsilon} \underbrace{\int_0^{R_c} R_l \cdot R_l\, r^2 dr}_{\equiv \text{Condition of normalization}} = 0$

Basis is created at fixed ϵ_l^v

$\Rightarrow$ easy to handle eigenvalue problem.

A_{lm} & B_{lm} are defined by conditions that basis must be continuous &

diffrantable.

LAPW ≡ most accurate method
- no frozen core approximation
- no shape approx. to v^{eff}, or $v(r)$

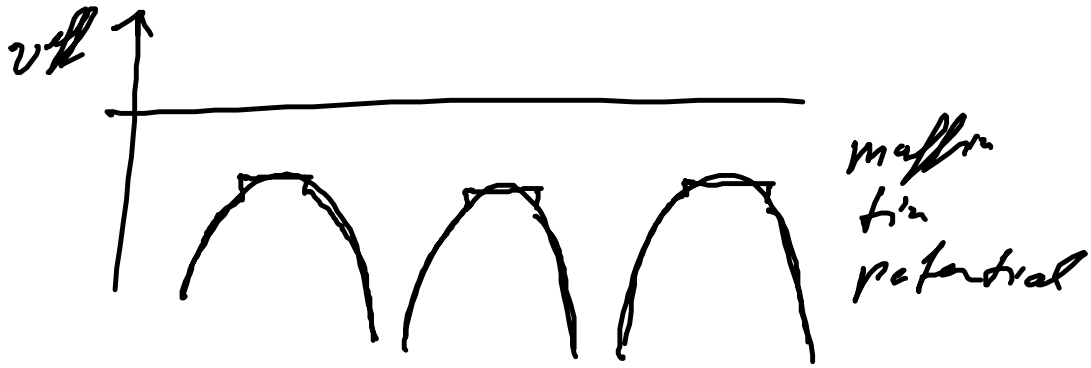
somewhat high CPU demand

No problem for simple solids.
but (costly) for surfaces & defects.

5.6.3 KKR and LMTO or ASW

Korring - Kohn - Rostoker
Linearized muffin orbital method (Olk. Andersen)
augmented spherical wave

KKR



Basis:

$$\chi_{lm}(\epsilon, \vec{r}-\vec{R}_I) = \begin{cases} R_l(\epsilon, |\vec{r}-\vec{R}_I|)\, Y_{lm}(\Omega_{r-R_I}) & \text{for } |\vec{r}-\vec{R}_I| \text{ inside sphere } I \\ \chi^{tail}(|\vec{r}-\vec{R}_I|)\, Y_{lm} & \text{otherwise} \end{cases}$$

diffent methods use diffent tails

KKR = $j_l(\kappa r)$, $h_l^{(1)}(\kappa r)$ Basis is energy dependent

LMTO: r^l, r^{-l-1}

ASW: $h^{(1)}(\sqrt{-\epsilon_l^v}\, r)$

5.7. Many body perturbation theory (beyond DFT).

Kohn-Sham → KS-eigenvalues

calculated bandstructures agree well with photoemission data — but

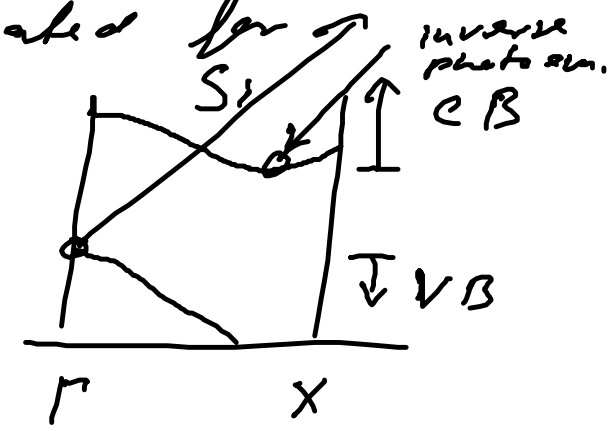
e.g. d-bands are typically too high

Biggest problem: For LDA (also GGA)

the KS bandgap of semiconductors and insulators is much smaller than experiment.

Potentials

KS bandstructure is evaluated for N-electron system.



Experiment

$N, N-1, N+1$

$$E^{g-p} = \epsilon_{CB}^{KS} - \epsilon_{VB}^{KS} + \Delta_{xc}$$

with

$$\Delta_{xc} = \lim_{\delta \to 0} \left(v^{xc}\Big|_{N+\delta} - v^{xc}\Big|_{N-\delta} \right)$$

E^{xc} has kinks when plotted as function of particle number N at integer values, i.e. at $N-1, N, N+1$

$\Rightarrow \frac{\delta E^{xc}}{\delta n}$ has discontinuities at integer values of particle number

very recent, high accurate treatments of xc show these kinks. LDA, GGA -- do not have these kinks.

We getting close to understand the
physics behind the kink
(W. Yang PRL, April 2008)
main reason for failure of LDA
to describe the band gap is the self-interaction
that is contained in the Hartree potential but not
corrected properly in the LDA.
Instead of "SI error" ≡ delocalization error.
the nature of an e^- in VB and in
the CB is very different.

How to deal with this problem?

⇒ many body perturbation theory

electron & hole are described by creation
and annihilation operators (also called field operator)

$\hat{\psi}^\dagger(\vec{r},t)$ ≡ Operator that creates an electron
at point $\vec{r}$ and time t.

$\hat{\psi}(\vec{r},t)$ ≡ annihilates an electron at
point $\vec{r}$ and time t.

The single particle Green function of a many body
problem:

$$G(\vec{r},\vec{r}',t,t') = -i\langle N|\hat{T}\{\hat{\psi}(\vec{r},t)\hat{\psi}^\dagger(\vec{r}',t')|N\rangle$$

$|N\rangle$ ≡ ground state of many-body problem
so far called Φ_0

$\hat{T}$: time ordering operator

$$\hat{T}\ \hat{\psi}(\vec{r},t)\,\hat{\psi}^{\dagger}(\vec{r}',t') =$$

if $t > t'$ $\quad = \hat{\psi}(\vec{r},t)\,\hat{\psi}^{\dagger}(\vec{r}',t')$

if $t' > t$ $\quad = -\hat{\psi}^{\dagger}(\vec{r}',t')\,\hat{\psi}(\vec{r},t)$