

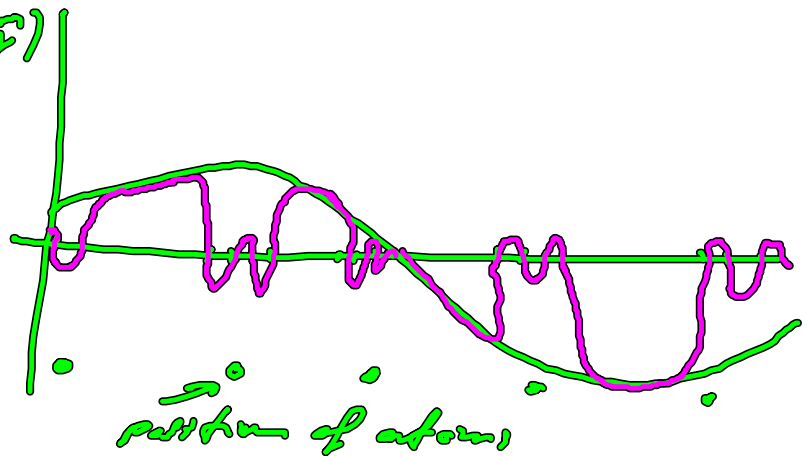
5.6 Other methods for solving the Schrodinger equation for periodic crystal

Solow & nearly free electron
27 LC 40

Truth is intermediate $\text{Re } \psi_n(\vec{r})$

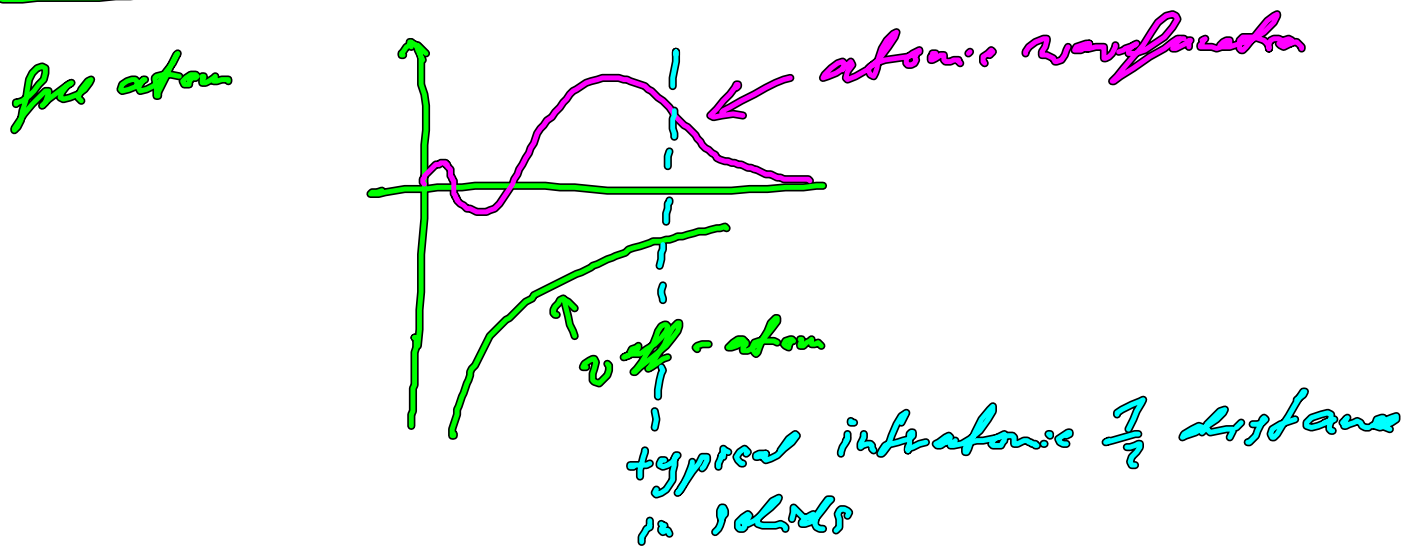
close to nuclei the wave function looks atomic like.

Somewhat away from nuclei it is smooth.



close to nuclei: by gradient;
high kinetic energy

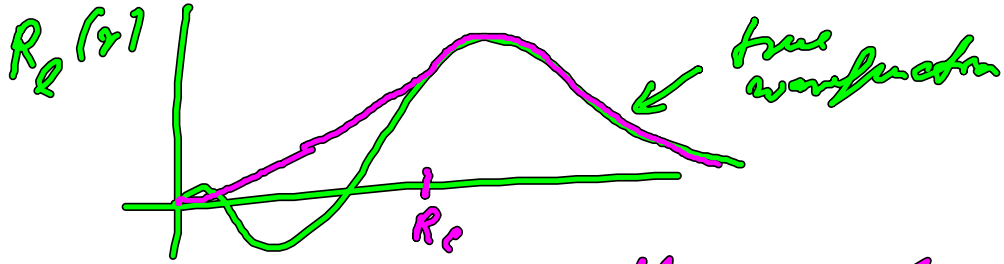
5.6) Pseudopotential method



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

\uparrow extent of core state

\Rightarrow replace $v_{\text{eff-atom}}$ by $v_{\text{eff-pseudo}}$
where $v_{\text{eff-pseudo}}$ has orbitals without oscillations



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

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

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

How to do this

1) calculate φ^{atom}

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

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

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

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

"most Schrödinger eqn."

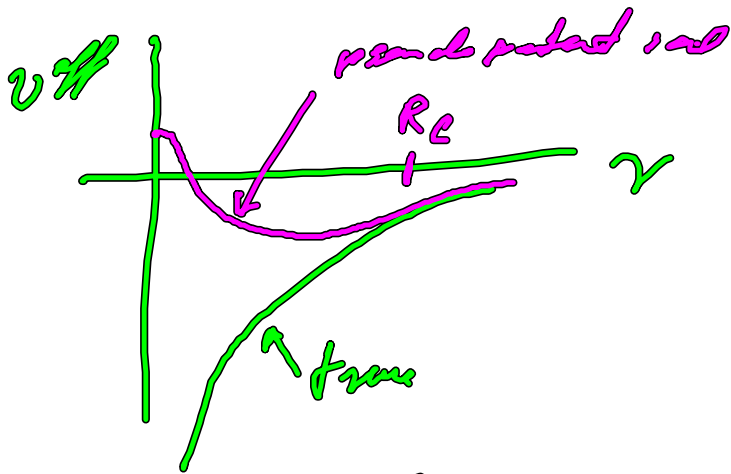
4) construct $\underline{v^{\text{pseudo}}}$ = input for a self-consistent Kohn-Shan eqn.

$$= v^{\text{eff-pseudo}} - v^{\text{Hartree}}[\varphi^{\text{pseudo}}]$$

v^{pseudo} & v^{eff} - pseudo
or non l -dependent

$$-v^{\text{xp}} [u^{\text{pseudo}}]$$

$$v^{\text{pseudo}} = \sum_l v_l^{\text{pseudo}} |l\rangle \langle l|$$



divergence at $r=0$
is gone.

An expansion of
hamiltonian and
wavefunction in
plane wave is efficient

Properties of all into pseudo potentials

- 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 $E = E_0$ and in the neighborhood $E = E_0 \pm \Delta$ the scattering properties of true & pseudo potentials agree.

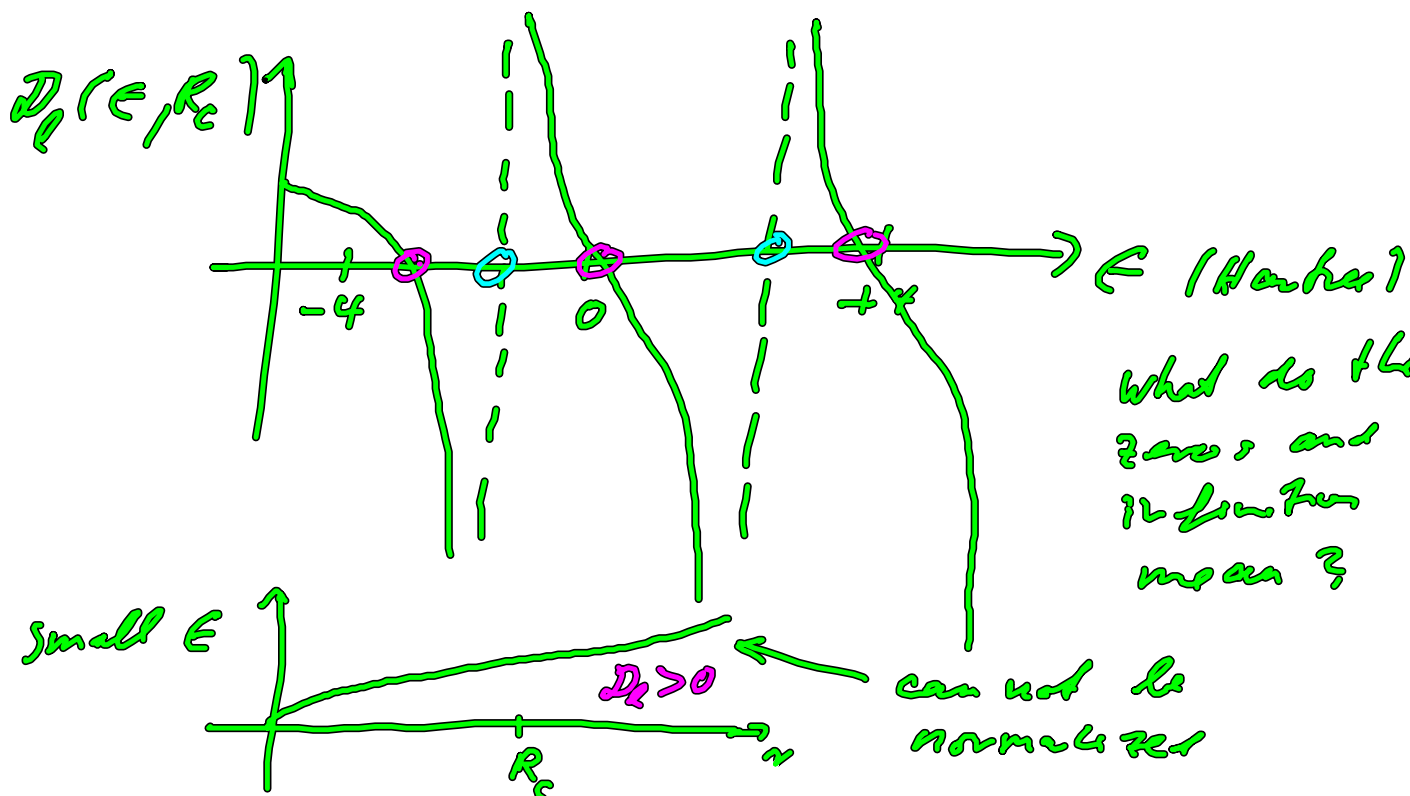
Logarithmic derivative

$$D_l(E, \hat{R}) \stackrel{!}{=} \frac{1}{r} \frac{d \ln R_l(E, r)}{d \ln r} \Big|_{r=\hat{R}}$$

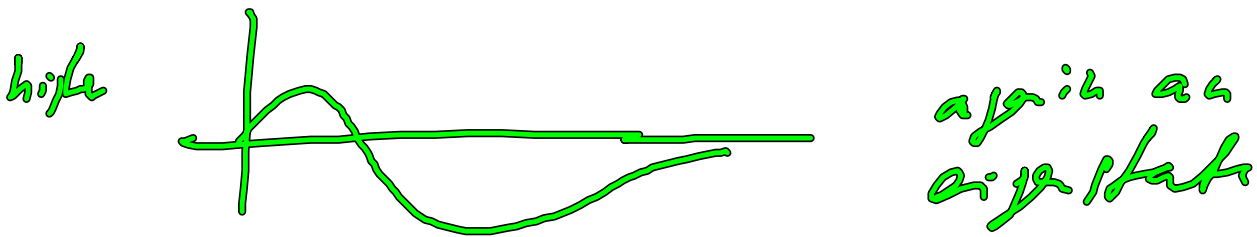
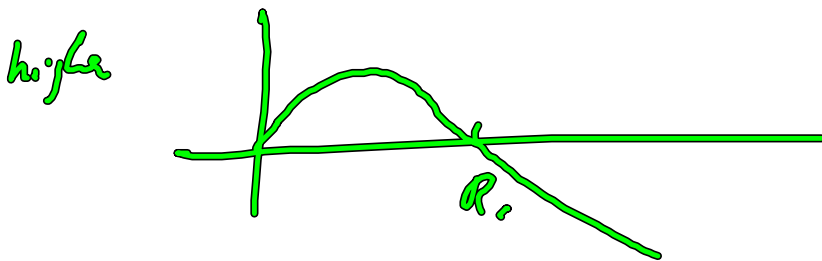
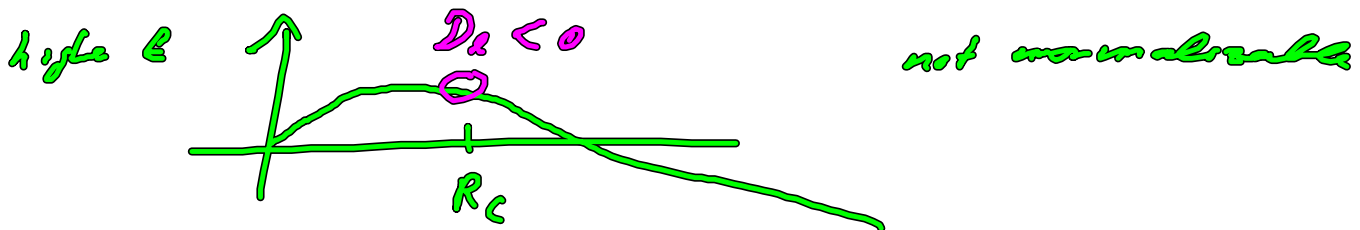
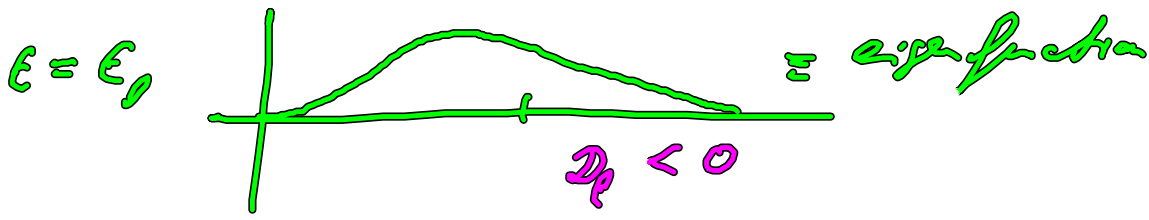
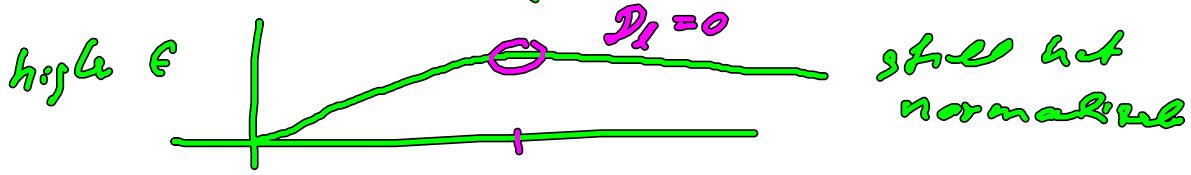
$$= \frac{R_l'(E, r)}{R_l(E, r)} \Big|_{r=\hat{R}}$$

R_l = radial wave function
 \hat{R} = Radius larger than R_c

$$\frac{d D_l^{\text{pseudo}}}{d E} \Big|_{E=E_0} = \frac{d D_l^{\text{true}}}{d E} \Big|_{E=E_0}$$



What do these zeros and infinities mean?



Problem of the pseudopotential approach

1) frozen core approx.

(core states cannot adjust to new environment)

2) pseudization

for $r < R_c$ potential & wavefunction are not correct.

3) treatment of xc taken values and core is not correct.

Typically ok.; 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 $r \leq R_c$)

- interstitial = space not covered by spheres.

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

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

Basiss set

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

$$\frac{\hbar^2}{2m} |\vec{k} + \vec{G}|^2 = E$$

best quality basis, but very inefficient.

Basis depends on ϵ

Matrix $\langle \chi_{\alpha}(\epsilon) | h | \chi_{\beta}(\epsilon) \rangle =$ energy dependent

$$h\psi = \epsilon\psi$$

Linear eigenvalue problem

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

LAPW

\equiv replace $\sum_{\alpha} g(\vec{k}, \vec{e}) R_{\alpha}(|\vec{r}-\vec{R}_{\alpha}|, \epsilon) \chi_{\alpha}$

$$\text{by } \sum_{\alpha} \left[A_{\alpha} R_{\alpha}(|\vec{r}-\vec{R}_{\alpha}|, \epsilon_{\alpha}^v) + B_{\alpha} \dot{R}_{\alpha}(|\vec{r}-\vec{R}_{\alpha}|, \epsilon_{\alpha}^v) \right] \chi_{\alpha}$$

ϵ_{α}^v
fixed energy

R_{α} and $\dot{R}_{\alpha} = \frac{d}{d\epsilon} R_{\alpha}(r, \epsilon)$ are linear

independent: $\int_0^{R_c} R_{\alpha} \cdot \dot{R}_{\alpha} r^2 dr = \frac{1}{2} \frac{\partial}{\partial \epsilon} \int_0^{R_c} R_{\alpha} \cdot R_{\alpha} r^2 dr = 0$

\equiv orth. normalization

Basis is created at

fixed ϵ_{α}^v

\Rightarrow easy to handle eigenvalue problem.

A_{α} & B_{α} are defined by conditions

that basis must be continuous &

Lippmann.

LAPW is most accurate method

- no frozen core approximation

- no shape approx. to v_{eff} , or $v(r)$

sometimes high CPU demand

No problem for simple solids.

but costly for surfaces & defects.

5.6.3 KKR and LMTO or APW


Korringa-Kohn-Rostoker

Linearized muffin orbital method (O.K. Anderson)

augmented spherical waves

KKR

v_{eff}



muffin
tin
potential

Basis:

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

different methods use different basis

$$\text{KKR} = j_l(xr), h_l^{(1)}(xr)$$

Basis is energy dependent

$$\text{LPTO: } r^l, r^{l-1}$$

$$\text{ASW: } h_l^{(1)}(\sqrt{-\epsilon_i} r)$$

5.7. Many body perturbation theory (beyond DFT)

Kohn-Shan \rightarrow KS-eigenvalues
calculated bandstructures agree well with
photoemitter data — but

e.g. d-bands are typically too high

Bigger problem: For LDA (or GGA)

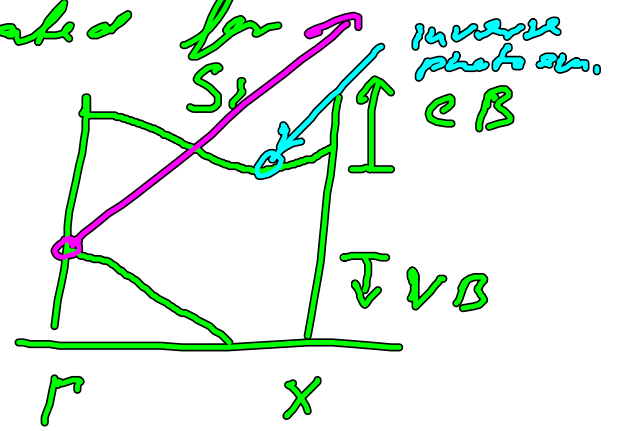
the KS bandgap of semiconductor and
insulator is much smaller than experiment.

delimita

KS bandstructure is evaluated for N -electron system.

$N, N-1, N+1$

approx



$$E^{xc} = E_{CB}^{KS} - E_{VB}^{KS} + \Delta_{xc}$$

with

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

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 accuracy 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" \equiv delocalization error.
The nature of an e^- in VB and in the CB is very different.

How to deal with this problem?

\Rightarrow Many body perturbation theory

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

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

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

The single particle Green function of a many body problem:

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

$|N\rangle \equiv$ ground state of many-body problem
So far called Φ_0

\hat{T} = time ordering operator

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

$$\text{if } t > t'$$

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

$$\text{if } t' > t$$

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