

# Chapter 6 continued - Practical DFT

$$\left[ -\frac{\nabla^2}{2} + v^{\text{nuc}}(\mathbf{r}) + v_{\text{es}}^e(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right] \phi_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}} \phi_{\mathbf{k}}(\mathbf{r})$$

Kohn-Sham Equations

$$n(\mathbf{r}) = \sum_{\mathbf{k}} f_{\mathbf{k}} |\phi_{\mathbf{k}}(\mathbf{r})|^2$$

$$E[n] = T_S[n] + \int d^3r v^{\text{nuc}}(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n]$$

However: not really linear Eq's in  $\phi_{\mathbf{k}}$ :

$$\left. \begin{aligned} v_{\text{xc}} &= \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})} \\ v_{\text{es}}^e &= \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \end{aligned} \right\} \begin{aligned} &\text{depend on } \{ \phi_{\mathbf{k}}(\mathbf{r}) \} \text{ as well} \\ &\Rightarrow \text{"self-consistent" solution needed} \end{aligned}$$

In practice:  $\rightarrow$  specify nuclear coordinates  $\{ \mathbf{R}_I \}$

$\rightarrow$  specify basis set  $\{ \phi_i \}$  to solve  $[\phi_{\mathbf{k}}(\mathbf{r}) = \sum_i c_{ki} \phi_i(\mathbf{r})]$

$\rightarrow$  choose level of approximation  $E_{\text{xc}}$

$\Rightarrow$  Route to total energies, electronic properties etc!

## 6.2 Boundary Conditions

• Molecules and Clusters in "empty" space

$\rightarrow$  specify  $\{ \mathbf{R}_I \} \rightarrow$  done.

• Solids, surfaces, molecular "wires", ...

$\rightarrow$  Periodic Boundary Conditions

Basic premise:  $v_S(\mathbf{r}) = v^{\text{nuc}}(\mathbf{r}) + v_{\text{es}}^e(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$

periodic

$$v_S(\mathbf{r} + \underline{T}_n) = v_S(\mathbf{r})$$

for all translations  $\underline{T}_n = n_1 \underline{a}_1 + n_2 \underline{a}_2 + n_3 \underline{a}_3$

$\underline{a}_1, \underline{a}_2, \underline{a}_3$  "lattice vectors"

$\underline{n} = (n_1, n_2, n_3)$  integer.

usually but not always  $\psi^{\text{wave}}(\underline{r})$  periodic if enough.

(not always; e.g., antiferromagnetism)

$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$

Bloch theorem: (only essence)

Eigenfunctions  $\varphi_{\underline{k}}(\underline{r})$  where  $\underline{k}$  "crystal momentum"

$$\varphi_{\underline{k}}(\underline{r} + \underline{T}_n) = e^{i\underline{k} \cdot \underline{T}_n} \varphi_{\underline{k}}(\underline{r})$$

can be written  $\varphi_{\underline{k}}(\underline{r}) = e^{i\underline{k} \cdot \underline{r}} \cdot u_{\underline{k}}(\underline{r})$

and  $u_{\underline{k}}(\underline{r}) = u_{\underline{k}}(\underline{r} + \underline{T}_n)$  periodic.

Reciprocal lattice:

$$\underline{k} \cdot \underline{T}_n \text{ appears in } \varphi_{\underline{k}}(\underline{r}) = e^{i\underline{k} \cdot \underline{T}_n} \varphi_{\underline{k}}(\underline{r}) \quad (*)$$

So if (\*) holds for  $\underline{k}$ , it also holds for any

$\underline{k} + \underline{G}_m$  if  $\underline{G}_m \cdot \underline{T}_n = 2\pi$  for all  $\underline{n}$ .

$\underline{G}_m$  can be found.

$$\text{Defining: } \underline{b}_1 = \frac{2\pi}{V_{\text{box}}} (\underline{a}_2 \times \underline{a}_3)$$

$$\underline{b}_2 = \frac{2\pi}{V_{\text{box}}} (\underline{a}_3 \times \underline{a}_1)$$

$$\underline{b}_3 = \frac{2\pi}{V_{\text{box}}} (\underline{a}_1 \times \underline{a}_2)$$

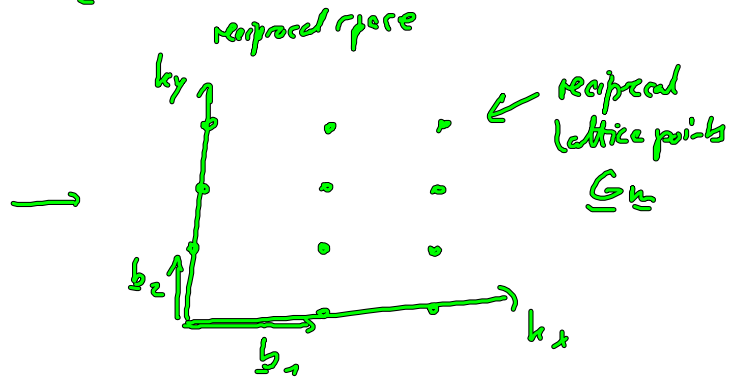
If we choose  $\underline{G}_m = m_1 \underline{b}_1 + m_2 \underline{b}_2 + m_3 \underline{b}_3$

then  $\underline{a}_i \cdot \underline{b}_j = 2\pi \delta_{ij}$

$\{\underline{b}_j\}$  define "dual space" to  $\{\underline{a}_1, \underline{a}_2, \underline{a}_3\}$

$\underline{G}_m$  is called reciprocal lattice

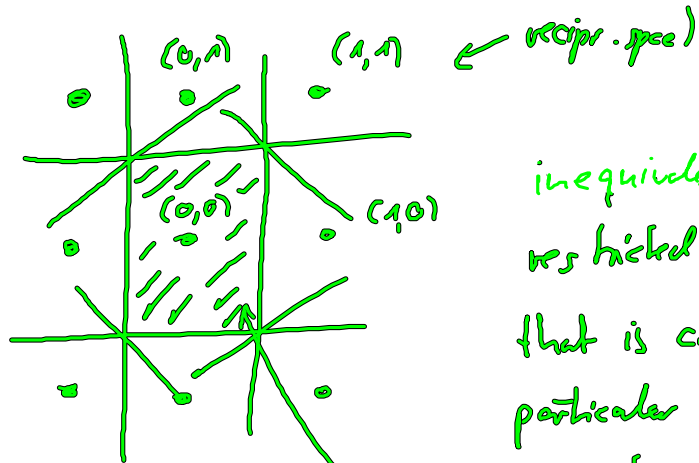
Restricts the space of inequivalent  $\underline{k}$ -vectors that we need to care about.



Upshot:

- Eigenfunctions  $\psi_{\underline{k}}$ ,  $\psi_{\underline{k}'}$  are independent of one another (orthogonal!)  
if  $\underline{k} \neq \underline{k}' + \underline{G}_m$

- Only  $\underline{k}$  in a part of reciprocal space not connected by any  $\underline{G}_m$  is relevant:



inequivalent  $\underline{k}$ -vectors restricted to a volume that is closer to one particular  $\underline{G}_m$  [(0,0)] than to any other!

"1st Brillouin zone"

At each  $\underline{k}$  point, can still seek

one or more Bloch functions  $u_{\underline{k}, n}(\underline{r})$

$n = 1, \dots$

↑  
"band index"

In a nutshell: Periodic systems

- Lattice vectors  $\{\underline{a}_i\}$

- Nuclear coordinates  $\{\underline{R}_I\}$  in the zeroth unit cell

How about a basis  $\{\varphi_i(\underline{r})\}$  defined for one unit cell?

$\Rightarrow$  Construct Bloch-like basis functions

$$\chi_{\underline{k},i}(\underline{r}) = \sum_{\substack{n \\ \uparrow \\ \text{unit cells}}} e^{i\underline{k}\underline{T}_n} \underbrace{\varphi_i(\underline{r} - \underline{T}_n)}_{\text{translated to unit cell } n}.$$

Since solutions  $\varphi_{\underline{k},n}(\underline{r})$ ,  $\varphi_{\underline{k}',n}(\underline{r})$  are orthogonal for  $\underline{k} \neq \underline{k}' \in 1st\ BZ$

$$\sum_{j=1}^S h_{ij}^{(\underline{k})} c_{nj}^{(\underline{k})} = E_{\underline{k},n} \sum_j s_{ij}^{(\underline{k})} c_{nj}^{(\underline{k})} \Rightarrow \text{separate eigenvalue for each } \underline{k}\text{-point.}$$

as usual  $h_{ij}^{(\underline{k})} = \int d^3r \chi_{\underline{k},i}^*(\underline{r}) \hat{h}_{\underline{k}s} \chi_{\underline{k},j}(\underline{r})$

$$n(\underline{r}) = \sum_{n=1}^S \int_{1.BZ} d^3k \int_{\underline{k},n} | \varphi_{\underline{k},n}(\underline{r}) |^2 \cdot \text{Normalization}$$

etc.

and similar BZ integrals for total energy expressions, etc.

$\rightarrow$  as soon as we define  $\{\varphi_i(\underline{r})\}$  Basis set

$\rightarrow$  Bloch's theorem does all the work.

For periodic systems, two concepts important.

(1) Band structure

Instead of  $\epsilon_{0k}$ ,  $k=1, \dots, N$ , (non-periodic!)

now have  $\epsilon_{k,0n} \equiv \epsilon_{0n}(k)$  continuous in  $k$ .

"Band structure"

→ extends over full 3D  $k$  space although usually plotted at high symmetry lines

→ In KS theory, direct meaning of  $\epsilon_{0n}(k)$  not rigorous, but obviously related to

- bonding
- K-space properties
- etc.

→ for solids, often good qualitative first approximation to experimental single-particle like levels, but straight KS eigenvalues can have severe limitations (e.g. LDA et al. underestimates any real band gap severely)

→ KS states  $\psi_{k,0n}$  can be used as starting points for MB perturbation theory (e.g. "GW") whose eigenvalues have physical meaning

(2) Density of states in BZ integrals

$$\int_{\text{BZ}} f(\epsilon(k))$$

↑  
some factor

convenient to write

$$\int d\epsilon g(\epsilon) f(\epsilon)$$

↑  
weight factor  
"counts" the number of states in interval  $\epsilon, \epsilon+d\epsilon$

$$g(\epsilon) = \int_{\text{BZ}} \sum_n \delta(\epsilon - \epsilon_n(k))$$

Important - sums up effect of all  $k$ -points, not just high symmetry lines!

## 6.3 Basis Sets: The All-Electron Problem

Set of functions  $\{\phi_i(r), i=1, \dots, S\}$  to expand orbitals  $\{\phi_{0k}(r)\}$

Ideally: • Choose generic, systematically convergent set  $\{\phi_i\}$

• Monitor  $n(r), E[n], \dots$  as we increase basis size  $S$  systematically until we declare "convergence".

For example: • Plane waves  $\frac{1}{\sqrt{V_{\text{box}}}} e^{ikr}$  up to  $k^2 \leq 2E_{\text{cut}}$  and increase  $E_{\text{cut}}$

• grid functions  $\delta(r-r_i)$ , grid spacing  $|\Delta r|$  finite and decrease  $|\Delta r|$  until "convergence"

(variants: - "Finite differences"  
- "Finite elements"  
- "Wavelets")

HOWEVER:

$$V^{\text{nuc}}(r) \sim \frac{Z_I}{|r - R_I|}$$

somewhat of a singularity.

• core electrons - tightly bound to nucleus  
- don't react much to chemical environment.

• valence electrons: extended, chemical bonding, response, etc..

→ "orthonormality wiggles" (rigid) near nucleus, very hard to expand in "simple" systematic basis.

Two generic strategies:

(1) deliberately incomplete basis set,  
attached and specially adapted near nucleus.

(2) "pseudoize away" the nucleus plus core electrons,  
focus on valence electrons outside nuclear region only.

## 6.4 Atom-centered basis sets (in principle, all-electron)

Many prescriptions - here, only a few!

- "Augmented plane waves"

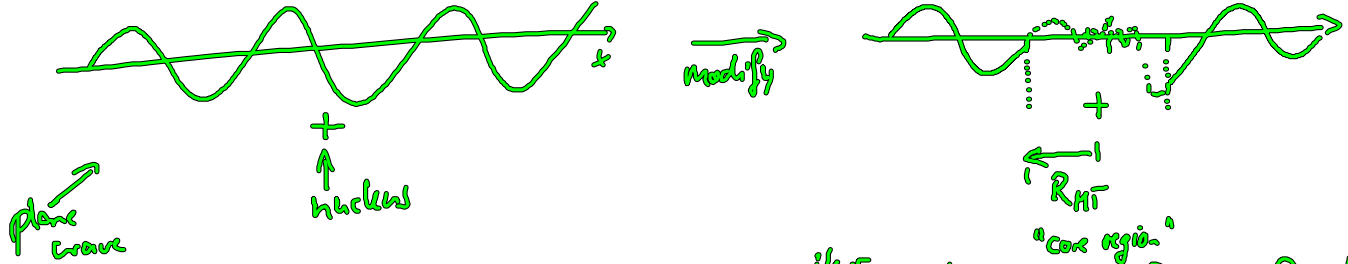
- Gaussian-type orbitals  $\sim (x-x_I)^l (y-y_I)^m (z-z_I)^n e^{-\alpha(r-R_I)^2}$

- Numeric atom-centered orbitals  $\phi_{nlm}(r-R_I) = \frac{u_{nl}(r-R_I)}{|r-R_I|} Y_{lm}(\Omega_I)$

- (Linearized) augmented plane waves

Slater 1937: Would like to use plane wave basis but undesirable.

$\Rightarrow$  modify plane waves to reflect correct behavior near the nucleus.



$$\varphi_{\mathbf{k}}^{\text{APW}} = \begin{cases} e^{i\mathbf{k}\cdot\mathbf{r}} & |\mathbf{r}-\mathbf{R}_I| > R_{MT} \text{ for all } I \\ \sum_{nlm} C_{nlm} \frac{u_{nl}(r)}{r} Y_{lm}(\Omega) & \text{inside core region} \end{cases}$$

solutions to exact radial Schrödinger Eq. inside core region

$C_{nlm}$  fitted to ensure continuity.

- plane wave part can be converged far valence! (chemistry)
- automatically correct behavior near nucleus.
- core electrons can be treated completely separately.

First real all-electron method for solids - benchmark method.

Numerically tricky in detail

- somewhat discontinuous at  $R_{MT}$
- different regions ↔ different numerical treatments
- Must make sure PW never see the nucleus
- BUT would still like to use Fast Fourier Transforms etc.