

Chapter 6 continued - Practical DFT

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

Kohn-Sham Equations

$$n(\mathbf{r}) = \sum_k f_k |\phi_{\alpha_k}(\mathbf{r})|^2$$

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

However: not really linear Eq's in ϕ_{α_k} :

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

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

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

\rightarrow choose level of approximation E_{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

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

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

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

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

usually but not always $V^{\text{net}}(\underline{r})$ 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:

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

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

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

\underline{G}_m can be found.

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

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

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

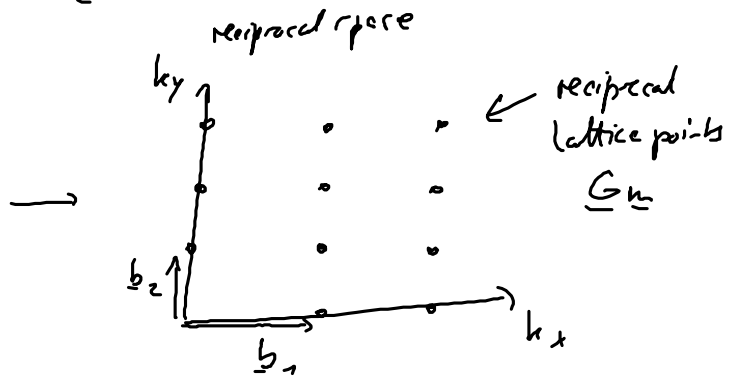
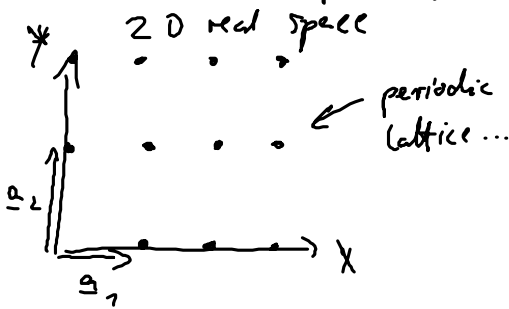
$$\text{If we choose } \underline{G}_m = m_1 \underline{b}_1 + m_2 \underline{b}_2 + m_3 \underline{b}_3$$

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.

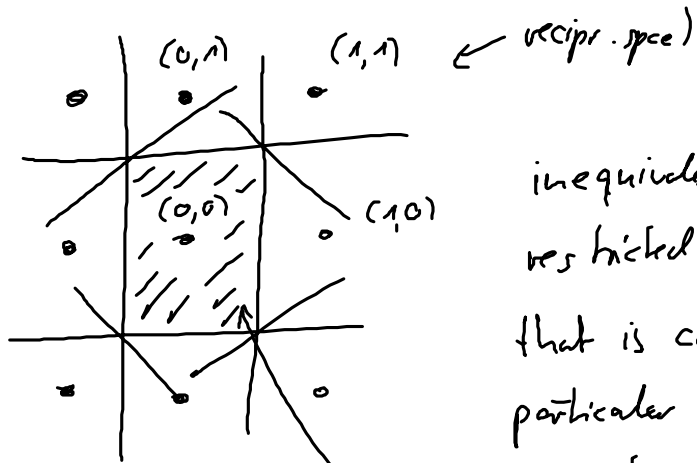


Upshot:

- Eigenfunctions $\phi_{\underline{k}}$, $\phi_{\underline{k}'}$ 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 covered 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

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

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

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

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

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

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 ϵ_{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
- response 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. underestimate any real band gap severely)

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

(2) Density of states in BZ integrals

convenient to rewrite

$$\int_{\text{BZ}} d^3k \underbrace{f(\epsilon(k))}_{\text{some function}} \longrightarrow \int d\epsilon \underbrace{g(\epsilon)}_{\text{weight factor}} f(\epsilon)$$

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

$$g(\epsilon) = \int_{\text{BZ}} d^3k \sum_n \delta(\epsilon - \epsilon_n(k))$$

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

6.3 Basis Sets: The All-Electron Problem

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

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

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

For example: • Plane waves $\frac{1}{\sqrt{V_{\text{base}}}} e^{i\mathbf{k}\cdot\underline{r}}$ up to $k^2 \leq 2E_{\text{cut}}$ and increase E_{cut}

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

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

HOWEVER:

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

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"

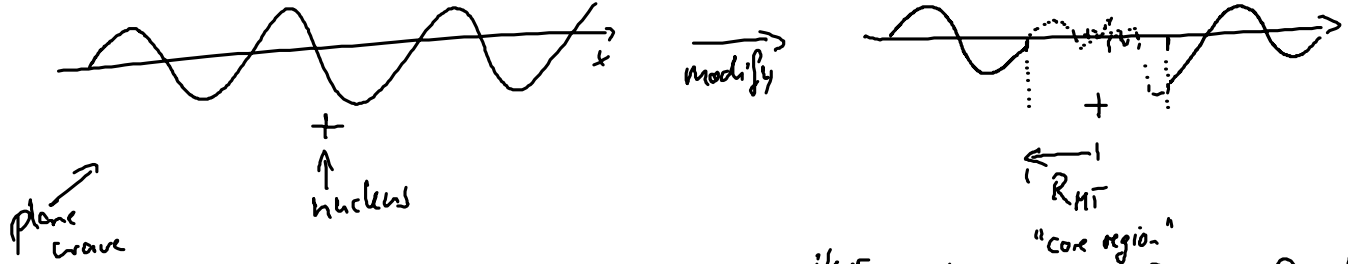
- Gaussian-type orbitals $\sim (x-x_I)^l (y-y_I)^m (z-z_I)^n e^{-\alpha(\underline{r}-\underline{R}_I)^2}$

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

- (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.



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

solutions to exact radial Schrödinger Eq. inside core region

C_{nlm} fitted to ensure continuity.

- plane wave part can be converged for 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.