

# Practical DFT continued

$$\left[ -\frac{\nabla^2}{2} + V^{\text{nuc}}(\mathbf{r}) + V_{\text{ex}}^e(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right] \phi_{0n}(\mathbf{r}) = \epsilon_{0n} \phi_{0n}(\mathbf{r})$$

$$\phi_{0n}(\mathbf{r}) = \sum_j c_{kj} \phi_j(\mathbf{r}) \quad j=1, \dots, S$$

Basis sets  $\{\phi_j(\mathbf{r})\}$ : must account for near nuclear region ("wiggles"!)

↳ (1) deliberately incomplete, crafted basis sets

(2) "pseudoize away" core electrons, near-nuclear "wiggles"

## 6.4 Atom-centered basis sets

• Augmented plane waves (Slater):

→ explicitly convergible in "valence region"

→ correct behaviour in core region enforced explicitly

• Gaussian-type orbitals

Boys, Shavitt (1950s):  $\phi_{lmn}^\alpha(\mathbf{r}) \sim x^l y^m z^n e^{-\alpha r^2}$

typ.  $L = l + m + n$  const. for a "basis fn"  
 $\alpha$  adjusted

$r, x, y, z$  really mean

$$|\mathbf{r} - \mathbf{R}_I|$$

$$x - x_I$$

etc. atom-centered

in principle equivalent  $\phi_{lmn}^\alpha(\mathbf{r}) \sim Y_{lm}(\Omega_I) r^L e^{-\alpha r^2}$

→ resembles eigenfunctions of harmonic oscillator

→ Lots of useful analytical properties:

$$1) \varphi_{lmn}^{\alpha}(\underline{r}) \sim x^l e^{\alpha x^2} \cdot y^m e^{\alpha y^2} \cdot z^n e^{\alpha z^2}$$

separable in  $x, y, z$

2) The product of two Gaussian-type orbitals (GTO's) is again a Gaussian!

$$e^{-\alpha(\underline{r}-\underline{R}_I)^2} \cdot e^{-\beta(\underline{r}-\underline{R}_J)^2} \sim e^{-\gamma(\underline{r}-\underline{R}_K)^2} e^{-\kappa(\underline{r}-\underline{R}_K)^2}$$

$$\text{where } \gamma = \frac{\alpha\beta}{\alpha+\beta}, \quad \kappa = \alpha+\beta, \quad \underline{R}_K = \frac{\alpha\underline{R}_I + \beta\underline{R}_J}{\alpha+\beta}$$

→  $\int d^3r \varphi_{lmn}^{\alpha}(\underline{r}-\underline{R}_I) \varphi_{l'm'n'}^{\beta}(\underline{r}-\underline{R}_J)$  known analytically

• kinetic energy  $-\frac{\nabla^2}{2} e^{-\alpha r^2} = \alpha(1-2\alpha r^2) e^{-\alpha r^2}$  again GTO with certain prefactors

•  $\int d^3r \varphi^{\text{GTO}}(\underline{r}-\underline{R}_I) \frac{1}{|\underline{r}-\underline{R}_K|} \varphi^{\text{GTO}}(\underline{r}-\underline{R}_J) =$

= ... many i-legal tricks (Szabo-Ostlund)

again analytically known

• Similar:  $\int d^3r d^3r' \frac{\varphi^{\text{GTO}}(\underline{r}-\underline{R}_I) \varphi^{\text{GTO}}(\underline{r}-\underline{R}_J) \varphi^{\text{GTO}}(\underline{r}'-\underline{R}_K) \varphi^{\text{GTO}}(\underline{r}'-\underline{R}_L)}{|\underline{r}-\underline{r}'|}$

⇒ All relevant ingredients analytically known

→ the rest is pre-tabulating

and matrix algebra (e.g. Exchange operator)

In practice: Hierarchies of element-dependent, pre-tabulated basis sets.  
(many such recipes)

Language (in principle):

- "minimal" basis  $\rightarrow$  one radial function for each  $1s, 2s, 2p$  valence angular momentum
- "Double-zeta + pol."  $\rightarrow$  minimal + 1 extra function with for each  $l$  + one more  $+ s, p, d$
- Triple-zeta  $+ s, p, d, f$
- ...

However, drawback (GTOs)

Real solution to Coulomb potential:  $u_{ne} \sim r^l e^{-\zeta r}$   
(e.g. H atom,  $1s$   $\zeta = 1$  in a.u.)  
"Slater-type orbital"

- incorrect tails
- incorrect behaviour near nucleus.

• Numeric Atom-Centered Orbitals (more general than GTO)

$$\phi_{num}(\mathbf{r}) = \frac{u_{ne}(r)}{r} \cdot Y_{lm}(\Omega) \quad r, \Omega \text{ w.r.t. a nuclear coord. } \underline{R}_I$$

if  $u(r)$  simply tabulated on grid (1D!)  
 $\rightarrow$  any shape possible

- near nuclear wiggles, tails: Simply use self-consistent free-atom radial functions as "minimal basis"
- Chemical bonding: Add "generic"  $u(r)$  on top  $\rightarrow$  tabulate for each element

→ systematic hierarchies possible.

(Double-zeta + pol., triple-zeta, ...)

Double-numeric + pol. etc.

- small basis sets for given accuracy
- can "converge" to essentially any accuracy if needed

Drawback:

Overlap integrals  $S_{ij}$

Hamiltonian  $H_{ij}$

Coulomb terms  $V_{es}^e(r)$

must all be found by numerical i-integrals  
(few analytical tricks)

→ high "prefactor" for  $O(N)$  operations

→ matrix algebra (K.S. eigen problem  
Hartree-Fock)

same scaling as Gaussians but smaller prefactor  
(smaller prefactor)

- many more out there!

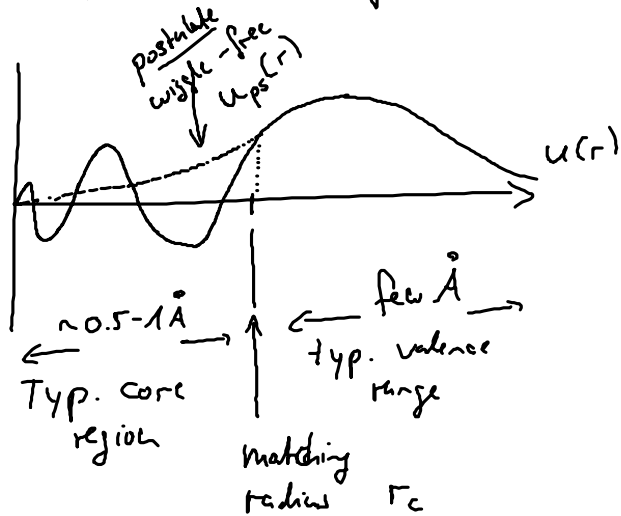
## 6.5. "Pseudization" - Getting rid of the nucleus

- Early realization:
- Core electrons mostly rigid around nucleus, even in molecules/solids
  - Valence electrons mostly responsible for chemical/materials properties

For many problems, we do not need core electrons - can we make them go away?

Example: "Norm-conserving pseudopotentials"

Consider typical valence  $u(r)$  for atoms



Now we have (for atom): 
$$u(r) = \begin{cases} U_{ps}(r) & r < r_c \\ u_{AE}(r) & r > r_c \end{cases}$$

at  $r_c$ , require continuity 
$$\frac{u'_{ps}(r)}{U_{ps}(r)} = \frac{u'_{AE}(r)}{u_{AE}(r)}$$

and norm-conservation: 
$$\int_0^{r_c} dr |U_{ps}(r)|^2 = \int_0^{r_c} dr |u_{AE}(r)|^2$$

But this much more friendly radial function is, sadly, not an eigenfunction to our atom.

To what is it an eigenfunction?

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{ps}(r) \right] U_{ps}(r) = \epsilon_{AE} U_{ps}(r)$$

↳ invert to find  $V_{ps}(r)$

If we substitute  $V_{ps}(r)$  for  $V^{nuc}(r)$ :

→  $V_{ps}(r)$  is eigenfunction

→ lowest state (nodless) ⇒ no more core electrons

→ reproduce free-atom eigenvalues for valence

→  $V_{ps}(r)$  is smooth, easy to handle.

Caveats: • for atoms, different  $l$  channels yield different  $U_l(r)$   
→ need separate pseudopotentials for each  $l$ !

In practice, must project:  $\hat{V}_{ps} = \sum_{lm} |lm\rangle V_{ps}^l(r) \langle lm|$   
non-local pseudopotential

no longer Hermitian!

→ must test to see that there are no unphysical ground states.

• sufficient "smoothness" matter → still approximate for  
very tight orbitals [2p for C, N, O etc

3d in TM

4f in rare earths]

• What if core states are not completely inert?

→ check PP calculations with AE

Construct and test PP very carefully.

Nonetheless: - Fasker's systematically convergible method around

- Many variants to patch detail

- more rigorous derivations possible.

## 6.6 Plane waves

$$\left[ -\frac{\nabla^2}{2} + V_{ps}^{loc}(\underline{r}) + \sum_{\underline{l} \neq \underline{k}} |l m\rangle V_{ps}^k \langle l m| + V_{ec}(\underline{r}) + V_{xc}(\underline{r}) \right] \varphi_{0k}^{ps}(\underline{r}) = \epsilon_{0k} \varphi_{0k}^{ps}(\underline{r})$$

Bloch theorem:

$$\varphi_{0k}(\underline{r}) = \varphi_{\underline{k}, 0n}(\underline{r}) = e^{i\underline{k} \cdot \underline{r}} \underbrace{u_{\underline{k}, n}(\underline{r})}_{\text{periodic function.}}$$

Simple Fourier transform  $u_{\underline{k}, n}(\underline{r}) = \sum_{\underline{G}} C_{\underline{k}, n}(\underline{G}) e^{i\underline{G} \cdot \underline{r}}$

if  $u_{\underline{k}, n}(\underline{r})$  periodic  $\Rightarrow$  only  $\underline{G}$  allowed that are part of reciprocal lattice.

$\Rightarrow$  obvious choice for basis function

$$\varphi_{\underline{G}}(\underline{r}) = \frac{1}{\sqrt{V_{\text{base}}}} \cdot e^{i\underline{G} \cdot \underline{r}}$$

or possibly dependent on  $\underline{k}$

$$\varphi_{\underline{G}}^{\underline{k}}(\underline{r}) = \frac{1}{\sqrt{V_{\text{base}}}} e^{i(\underline{k} + \underline{G}) \cdot \underline{r}}$$

How to make this finite?

Maximum Fourier component  $\frac{1}{2} |\underline{k} + \underline{G}|^2 \leq E_{\text{cut}}$  "cutoff energy"

or  $G_{\text{cut}} = \sqrt{2E_{\text{cut}}}$  at  $\Gamma$  ( $\underline{k} = 0$ )

Reciprocal lattice :  $|n_1 \underline{b}_1 + n_2 \underline{b}_2 + n_3 \underline{b}_3| \leq G_{\text{cut}}$

e.g. for orthogonal  $\{\underline{b}_i\} \equiv$  orthogonal  $\{\underline{a}_i\}$  in real space

$$n_i \geq \frac{G_{\text{cut}}}{|\underline{b}_i|} = \frac{G_{\text{cut}} |\underline{a}_i|}{2\pi} \geq n_i - 1$$

But: Fourier transforms can only resolve a finite length scale

$$\Delta x \cdot G_{\text{cut}} = 2\pi$$

$$\rightarrow \Delta x_i = \frac{|\lambda_i|}{n_i} \quad \text{is minimal resolvable real-space spacing for given } G_{\text{cut}}$$

Upshot: • PW expansion for given  $G_{\text{cut}}$  exactly equivalent to real-space grid representation with spacing  $\{\Delta x_i\}$

- FFT's make use exactly of this equivalence
- Can even estimate max. needed  $G_{\text{cut}}$  a priori from  $\psi_{\text{ps}}(r)$  when constructing atomic pseudopot'l.
- Can increase  $G_{\text{cut}}$  to  $\infty$  in practice because  $\phi_{\underline{G}}^{\text{ps}}(\underline{r})$  are exactly orthonormal.

In practice: Need matrix elements

$$\phi_{\underline{k}, \text{ps}}^{\text{ps}}(\underline{r}) = \sum_{\underline{G}} C_{\underline{k}, \underline{G}}(\underline{G}) \frac{1}{\sqrt{V_{\text{box}}}} e^{i(\underline{k} + \underline{G}) \cdot \underline{r}}$$

$\frac{1}{2} |\underline{k} + \underline{G}|^2 \leq E_{\text{cut}}$

$$\Rightarrow \text{kin energy: } T_{\underline{G}, \underline{G}'}^{\underline{k}} = -\frac{1}{2} \int d^3 r e^{-i(\underline{k} + \underline{G}) \cdot \underline{r}} \cdot \nabla^2 \cdot e^{i(\underline{k} + \underline{G}') \cdot \underline{r}}$$

$$= \frac{1}{2} |\underline{k} + \underline{G}|^2 \delta_{\underline{G}, \underline{G}'} \quad \underline{\text{diagonal}}$$

$$\text{potential (local only)} \quad V_{\underline{G}, \underline{G}'} = \frac{1}{V_{\text{box}}} \int d^3 r v_s(\underline{r}) e^{-i(\underline{G} - \underline{G}') \cdot \underline{r}} \cdot \underbrace{e^{-i(\underline{k} - \underline{k}') \cdot \underline{r}}}_1$$

$$=: \tilde{v}_s(\underline{G} - \underline{G}') \quad \text{Fourier component of the potential.}$$



and ultimately:

$$\sum_{\underline{G}'} \left( \frac{1}{2} |\underline{k} + \underline{G}|^2 \delta_{\underline{G}, \underline{G}'} + \tilde{V}_s(\underline{G} - \underline{G}') \right) C_{\underline{k}, n}(\underline{G}) = \epsilon_{\underline{k}, n} C_{\underline{k}, n}(\underline{G})$$