

Practical DFT continued

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

$$\varphi_{\alpha_k}(\mathbf{r}) = \sum_j c_{kj} \varphi_j(\mathbf{r}) \quad j=1, \dots, S$$

Basis sets $\{\varphi_j(\mathbf{r})\}$: 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 convergent in "valence region"

→ correct behaviour in core region enforced explicitly

• Gaussian-type orbitals

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

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

r, x, y, z really mean

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

$$x - x_I$$

etc. atom-centered

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

→ 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

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

= ... many i-legendre tricks (Sato-Ostlund)

again analytically known

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

⇒ 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 l_s, l_p, l_d value angular momentum
- BUT NEED LINEAR COMBINATIONS TO APPROX REAL AT. ORB.
- "Double-zeta + pol." \rightarrow minimal + 1 extra function min for each l + one more + s, p, d
- Triple-zeta + s, p, d
- ...

However, drawback (GTOs)

Real solution to Coulomb potential: $u_{nl} \sim r^l e^{-\zeta r}$
(e.g. Hydrogen, $l_s \zeta = 1$ in a.u.)
"Stato-type orbital"

- incorrect tails
- incorrect behaviour near nucleus.

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

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

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

Drudeck:

Overlap integrals	S_{ij}
Hamiltonian	H_{ij}
Coulomb terms	$V_{es}^e(\epsilon)$

must all be found by numerical 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!

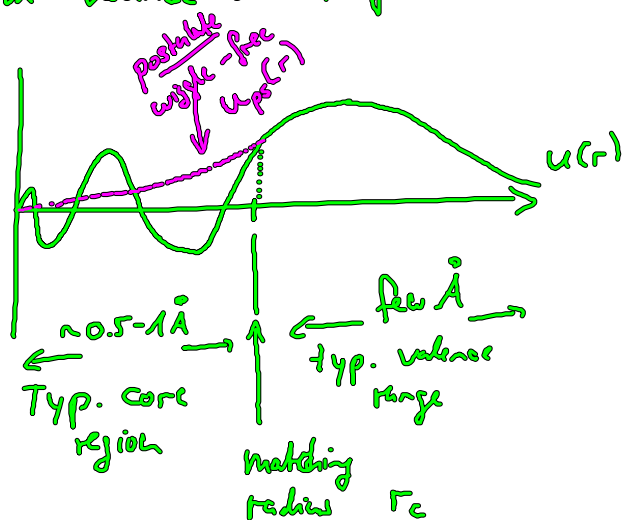
6.5. "Pseudization" - Getting rid of the nucleus

- 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 values

→ $V_{ps}(r)$ 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.

Nevertheless: - Faskits systematically convergible method around

- Many variants to patch detail

- more rigorous derivations possible.

6.6 Plane waves

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

Bloch theorem:

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

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

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

\Rightarrow obvious choice for basis function

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

or possibly dependent on \underline{k}

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

How to make this finite?

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

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

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

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

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

But: Fourier transforms can only resolve a finite length scale

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

$$\rightarrow \Delta x_i = \frac{|a_i|}{h_i}$$

is minimal resolvable real-space spacing for given G_{cut}

Upshot: • PW expansion for given G_{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_{cut} a priori from $\psi_{\text{ps}}(r)$ when constructing atomic pseudopot'l.
- can increase G_{cut} to ∞ in practice because $\phi_{\underline{G}}^{\text{ps}}(\underline{r})$ are exactly orthonormal.

In practice: Need matrix elements

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

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

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

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

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

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

and ultimately:

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