

(Local) Basis sets in computational chemistry

Furio Cora
f.cora@ucl.ac.uk
Chemistry 125

The ultimate goal:

Solve the Schrödinger equation

$$H\Psi = E\Psi$$

or

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V \right\} \Psi(r) = E\Psi(r)$$

for a many-electron system,
possibly a crystalline solid described under PBC.

Impossible without approximations:

Born-Oppenheimer

Mean field (independent particles): HF and KS-DFT

1-electron Hamiltonian

$$H_{elec} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} = \sum_{i=1}^N h(x_i)$$

Mean field: replace $1/r_{ij}$ with $v(x_j)$ – average field created by all other electrons on the reference i -th electron

$$f(x_i) = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v^{HF}(x_i)$$

Solutions (eigenstates) of the 1-electron Hamiltonian describe 1-electron states of the system (orbitals): $\chi(x_j)$

$$f(x_i) \chi(x_i) = \varepsilon \chi(x_i)$$

The HF solution: N-e wavefunction

N-electron state = product of N occupied 1-electron states

$$\Psi_{HP}(x_1, x_2, \dots, x_N) = \chi_i(x_1) \chi_j(x_2) \dots \chi_k(x_N)$$

Built into Slater determinant to satisfy Fermi statistics (wavefunction antisymmetric for exchange of 2 e)

$$\Psi(x_1, x_2, \dots, x_N) = (N!)^{-1/2} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \dots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \dots & \chi_k(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \dots & \chi_k(x_N) \end{vmatrix}$$

This leads to calculated energy

$$E_{elec}(\{\chi_a\}) = \langle \Psi_{elec} | H_{elec} | \Psi_{elec} \rangle$$

Includes complex many-centre integrals:

$$E_{elec} = \langle \chi_1 \chi_2 \cdots \chi_N | \underbrace{\sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} \right)}_{1e} + \underbrace{\sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}}_{2e} | \chi_1 \chi_2 \cdots \chi_N \rangle$$

and

$$E_{elec} = \sum_{a=1}^N \int dx_1 \chi_a^*(x_1) h_{one}(x_1) \chi_a(x_1) + \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N \left[\int dx_1 dx_2 \chi_a^*(x_1) \chi_a(x_1) r_{12}^{-1} \chi_b^*(x_2) \chi_b(x_2) - \int dx_1 dx_2 \chi_a^*(x_1) \chi_b(x_1) r_{12}^{-1} \chi_b^*(x_2) \chi_a(x_2) \right]$$

One-electron: kinetic energy and e-nuclei Coulomb

Two-electron: e-e Coulomb and exchange

The Kohn-Sham DFT solution: N-e density

Fictitious system of independent electrons

1-electron states of the system (orbitals): $\chi(x_i)$

Used only to calculate the total density

$$\rho_S(\mathbf{r}) = \sum_i |\chi_{KS}^2(\mathbf{r})| = \rho_{exact}(\mathbf{r})$$

Energy is a functional of the total electron density

Approximations hidden in the exchange and correlation (xc) functional

$$E_{\text{tot}}^{\text{KS}} = \sum_{\sigma=\alpha,\beta} \sum_{i=1}^{N_\sigma} n_{\sigma i} \langle \varphi_{\sigma i} | -\frac{1}{2} \hat{\Delta} | \varphi_{\sigma i} \rangle + \int v_{\text{ext}}(\vec{r}) \rho(\vec{r}) d\vec{r} + \frac{1}{2} \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho_\alpha, \rho_\beta]$$

Kinetic Energy

Nuclear (external) potential

Coulomb energy

Exchange-correlation energy

Electron-electron interaction

ρ = TOTAL EL. DENSITY

Periodic Boundary Conditions

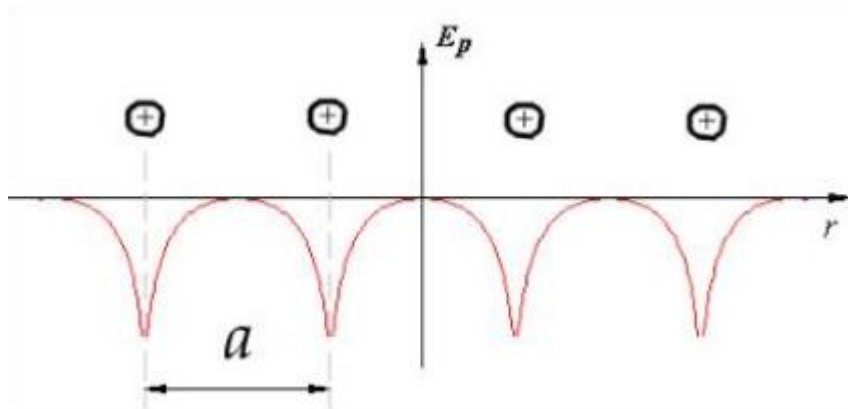
Wavefunction must satisfy Bloch's theorem.

In a periodic potential $u(\mathbf{r}) = u(\mathbf{r} + \mathbf{R})$ the eigenstates of H are the product of a function with same periodicity R , modulated by a wave of vector \mathbf{k}

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi(\mathbf{r})$$

The wavefunction is also periodic

$$|\psi(\mathbf{r} + \mathbf{R})|^2 = |\psi(\mathbf{r})|^2$$



Why a basis set?

The HF or KS expressions remain abstract

To evaluate the properties of a system we must have a numerical expression of orbitals/wavefunction/density

Expand them in a series of functions $\{\phi_\mu\}$ that describe the cartesian space (x,y,z) where electrons reside

Hilbert space

$$\psi_i = \sum_{\mu=1}^K C_{\mu i} \phi_\mu, \quad i = 1, 2, \dots, K$$

Ideally a **complete** basis set:

no constraint imposed on shape of 1e states

But this means infinite \rightarrow new approximations

Which functional form?

Compromise between accuracy and cost

- Makes chemical sense: good solution with few functions
- Makes mathematical sense: all HF or DFT expressions easy to calculate:

2-e integrals in HF (4 centres)

$$\int dx_1 dx_2 \chi_a^*(x_1) \chi_b(x_1) r_{12}^{-1} \chi_b^*(x_2) \chi_a(x_2)$$

and DFT (2 centres)

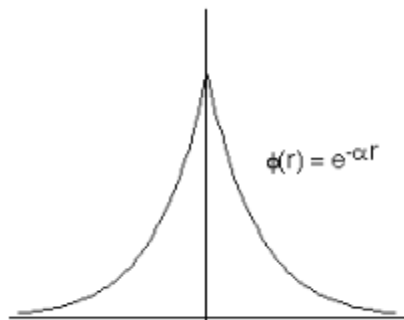
$$\frac{1}{2} \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho] = 0$$

Chemical choice 1: STO

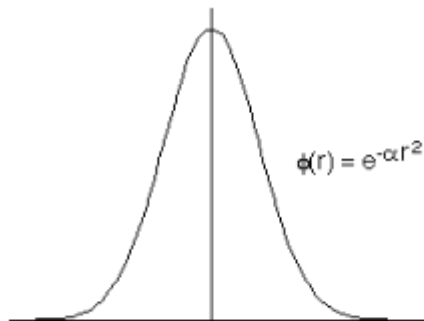
Refer to solutions of H atom (1e system), the only system known exactly.

Exact solutions are the Slater orbitals:

Exponential decay from nucleus $e^{-\zeta r}$



Slater-type 1s orbital



Gaussian-type 1s orbital

But!

Many centre integrals
are non analytical

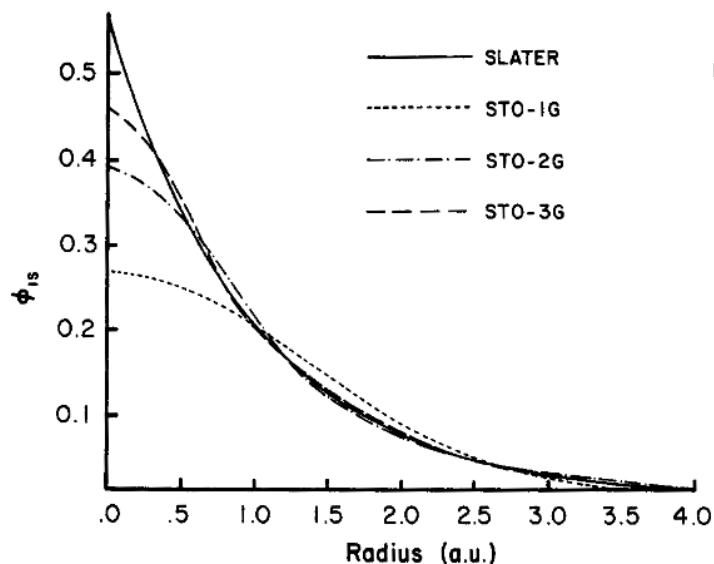
→ Few functions,
Complex maths
Numerical integration

Chemical choice 2: GTO, STO-nG

Replace Slater orbitals with Gaussian functions: e^{-ar^2}

Analytical integrals, but cusp on nucleus not reproduced

Compromise: use “contraction” (linear combination) of several Gaussian functions (primitives) → STO-nG



$$\text{STO-nG} = \sum_{i=1}^n c_i \exp(-a_i r^2)$$

Cusp more critical for core electrons

Number of contracted Gaussians varies with principal quantum number

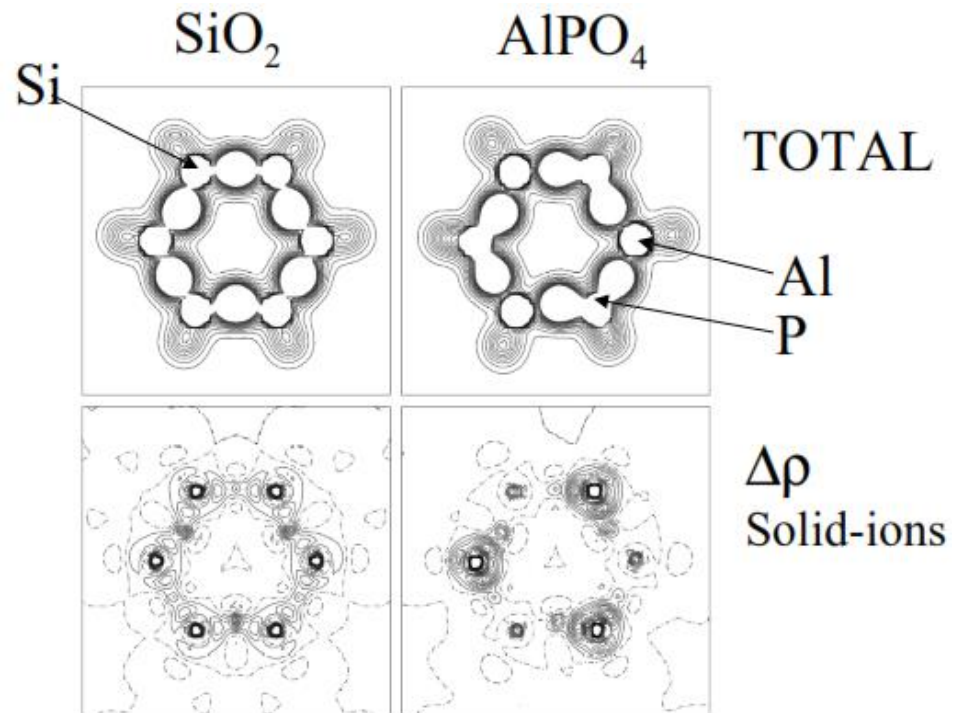
Figure 3.3 Comparison of the quality of the least-squares fit of a 1s Slater function ($\zeta = 1.0$) obtained at the STO-1G, STO-2G, and STO-3G levels.

Chemical choice 3: MO-LCAO

Assume that STOs and their mimic STO-nG are still a good representation for the many electron system; AOs. Molecular or crystalline orbitals obtained as LCAOs.

Few AOs often enough for accurate representation of molecular/crystalline electronic states

Must have (variational) flexibility in describing electronic redistribution in molecule/solid.



Hierarchy of STOs

Associated with atoms (can be expanded, e.g. bonds/vacancies)

Minimal: 1 basis function for each occupied AO in the atom

Double zeta: 2 basis functions for each AO

Triple zeta: 3 basis functions for each AO

Quadruple (QZ), 5Z, 6Z etc

Having differently sized functions allows MOs (COs) to get bigger/smaller in response to chemical changes.

Better variational flexibility.

Split valence: 2 basis functions for valence AOs only.

Core orbitals described by 1 function only

Triple valence: 3 basis fcts for valence AOs, 1 for core.

Electronic redistribution more pronounced for valence e-
less so for core states (changes in core described by valence AOs)

Hierarchy of STOs

Examples

H atom, Minimal BS: 1 AO (1s)

C,N,O atom, Minimal BS: 5 AO (1s, 2s, 2p_{x,y,z})

C,N,O atom, Double zeta: 10 AO (2*(1s, 2s, 2p_{x,y,z}))

C,N,O atom, Split valence: 9 AO (1s, +2*(2s, 2p_{x,y,z}))

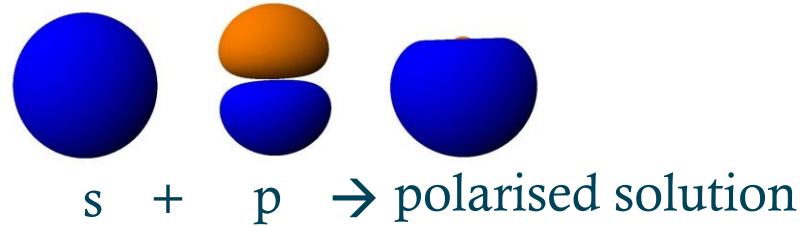
“manageable numbers”

O(100) atoms system ~ O(1000) AOs

For STO-nG we count the contracted STOs,
not the primitive Gaussian functions (coefficients c_i
do not change)

$$\text{STO-nG} = \sum_{i=1}^n c_i \exp(-a_i r^2)$$

Hierarchy of STOs



Polarisation functions:

AOs with angular momentum ℓ higher than highest occupied in the atomic configuration, e.g. p AOs for H, d AOs for O etc

Allow atomic density to deform in the molecular/crystalline field. Indicated with star (*) in the BS acronym

Diffused functions:

Gaussians with very low exponent ($a < 0.05$)

Describe slow decay of wavefunction away from nucleus (STO varies more slowly than GTO). E.g. anions. Indicated with plus (+) in the BS acronym.

Anatomy of a Basis Set: H atom, STO-3G

A basis set of Contracted Gaussian-Type Orbitals (CGTO's) needs to specify the exponents (ζ_i 's) and the contraction coefficients (c_i 's). These are given below in the format used by the Gaussian program (exponents first)

```
H    0
S    3    1.00
      3.42525091      0.154328970
      0.623913730      0.535328140
      0.168855400      0.444634540
```

Anatomy of a Basis Set: C atom, STO-3G

```
C      0
S      3      1.00
        71.6168370          0.154328970
        13.0450960          0.535328140
        3.53051220          0.444634540
SP     3      1.00
        2.94124940          -0.999672300E-01          0.155916270
        0.683483100          0.399512830          0.607683720
        0.222289900          0.700115470          0.391957390
```

STO-3G and other basis sets by John Pople use “SP” shells, which share exponents for s and p functions

STO People's Notation: X-YZ G (+*)

Can use contractions of different size for core and valence electrons

X: indicates number of primitive Gaussians for core AOs

Y: nr primitive G' for inner valence AOs

Z: nr primitive G' for inner valence AOs

} Split valence BS

* for polarisation functions

(sometimes ** to differentiate H from heavy atoms)

+ for diffused functions

First systematic BS proposed by John Pople (Nobel prize 1998)

e.g. STO-3G, 6-31G, 6-311G** or 6-311G(d,p)

STO Dunning's Notation: (*ls,mp,nd*)/[*xs,yp,zd*]

l primitive s functions, contracted into *x* AOs of s type
m primitive p functions, contracted into *y* AOs of p type, etc

e.g. People's 6-311G(d,p) for C:

6+3+1+1 primitive s functions, contracted into 4

3+1+1 p 3

1 d 1 (polarisation)

Indicated as (11s,5p,1d)/[4s,3p,1d]

Matrix notation

Once a basis set $\{\phi_\mu\}$ is chosen, the Schrödinger eqn can be expressed in matrix form

$$f(r_1)\psi_i(r_1) = \varepsilon_i\psi_i(r_1)$$

$$\psi_i = \sum_{\mu=1}^K C_{\mu i} \phi_\mu, \quad i = 1, 2, \dots, K$$

$$f(r_1) \sum_{\nu} C_{\nu i} \phi_\nu(r_1) = \varepsilon_i \sum_{\nu} C_{\nu i} \phi_\nu(r_1)$$

Multiply by ϕ_μ^* and integrate:

$$\sum_{\nu} C_{\nu i} \int dr_1 \phi_\mu^*(r_1) f(r_1) \phi_\nu(r_1) = \varepsilon_i \sum_{\nu} C_{\nu i} \int dr_1 \phi_\mu^*(r_1) \phi_\nu(r_1)$$

$$FC = SC\varepsilon$$

Matrix notation

$$FC = SC_{\varepsilon}$$

AO-like basis sets $\{\phi_{\mu}\}$ are not orthonormal
Overlap matrix $\mathbf{S} \neq \mathbf{I}$

Solution requires to invert \mathbf{S}

$$\mathbf{F}^{\alpha'} = (\mathbf{S}^{-1/2})^T \mathbf{F}^{\alpha} \mathbf{S}^{-1/2}$$

$$\mathbf{C}^{\alpha} = \mathbf{S}^{-1/2} \mathbf{C}^{\alpha'}$$

Limitations of local basis sets

1. Over-complete – convergence to full basis set limit is unclear
Adding a new basis function does not always improve quality of results
2. Balance – similar quality for all atoms of the system
3. For large basis sets we can have linear dependencies
4. Basis set superposition error (BSSE)
Interaction between sub-systems A+B overestimated
basis set of (A+B) better than that of A and B isolated
5. Best choice of basis set of given size is not unique
Many careers devoted to basis set development

Convergence of calculated properties vs basis set

Depends on property. Example energy and geometry of diatomic molecules in HF calculations

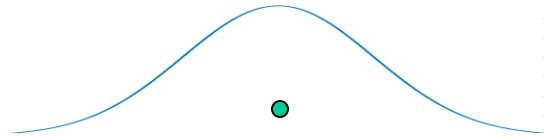
Basis Set	Total Energy / Hartree		
	H ₂	N ₂	H ₂ O
STO-3G	-1.117	-107.496	-74.963
4-31G	-1.127	-108.754	-75.907
6-31G*	-1.131	-108.942	-76.023
HF-limit	-1.134	-108.997	-76.065

Basis	Bond Length / Å				
	H ₂	N ₂	CO	NH ₃	H ₂ O
STO-3G	0.712	1.134	1.146	1.033	0.989
medium	0.732	1.079	1.113	1.004	0.947
HF-limit	0.733	1.065	1.101	0.999	0.939
Experiment	0.741	1.097	1.128	1.011	0.957

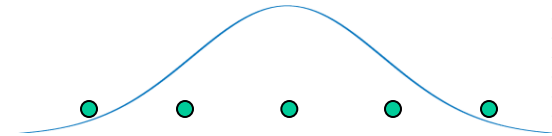
Excited states, derivatives of E or ρ (e.g. polarizability), correlation, more difficult to converge

Local basis sets for crystalline solids

1. Avoid diffused functions (exponent < 0.1)
Needed in molecules to describe decay of density/WF
no “outer space” in crystals



molecule

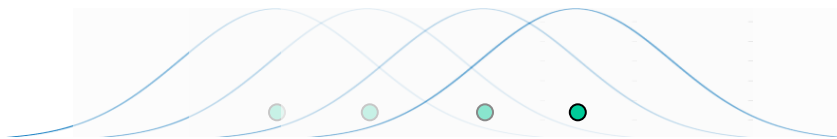


crystal (no point far from one atom)
cooperative effects

Numerical instability: when exponent $\rightarrow 0$
overlap from neighbouring atoms is similar; $|S| \rightarrow 0$

$$FC = SC\varepsilon$$

Solution requires to invert S



Local basis sets for crystalline solids

AOs do not satisfy Bloch's theorem.

Build Bloch fcts as Fourier transform of the AOs

$$\varphi_i(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}} \exp(i\mathbf{k}\mathbf{R}_{\mathbf{n}}) \chi_i(\mathbf{R}_{\mathbf{n}} + \mathbf{r} - \mathbf{r}_i)$$

$\mathbf{R}_{\mathbf{n}}$ = lattice vector; χ_i = i -th AO in the cell centred in \mathbf{r}_i

Bloch fcts $\{\varphi_i\}$ extend over infinite lattice described by PBC

$$\chi_i(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{n}} C_{i\mathbf{n}} \varphi_{i\mathbf{n}}(\mathbf{k}, \mathbf{r})$$

$$H \chi_i(\mathbf{k}, \mathbf{r}) = E_i(\mathbf{k}) \chi_i(\mathbf{k}, \mathbf{r})$$

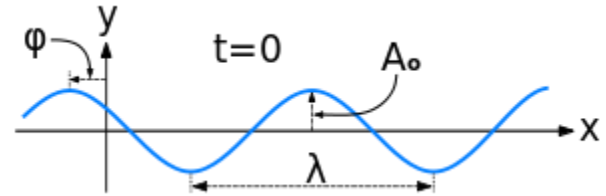
Hamiltonian depends on \mathbf{k}

?

$$FC = SC\varepsilon \quad \longrightarrow \quad F(\mathbf{k})C(\mathbf{k}) = S(\mathbf{k})C(\mathbf{k}) \quad (\mathbf{k})$$

Mathematical choice : Planewaves

$$U(\mathbf{R}) = U_o e^{-i(\mathbf{K} \cdot \mathbf{R})}$$



Resolve most issues of local basis sets:

- Orthonormal (no need to invert S)
adding new PWs systematically improves solution
K is an energy \rightarrow energy cutoff (reciprocal lattice points K)
- Satisfy Bloch's theorem (PBC)
- Maths trivial
- No BSSE

but!

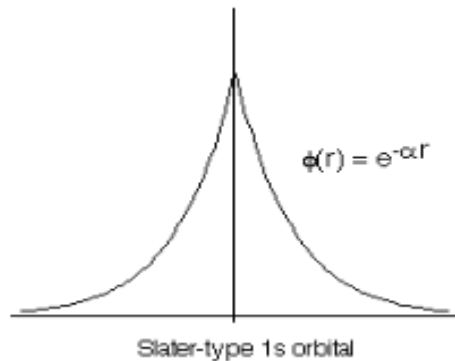
Have no resemblance to real electron density/wavefunction

Millions PWs needed

Difficult to extract “chemistry” from PW expansion

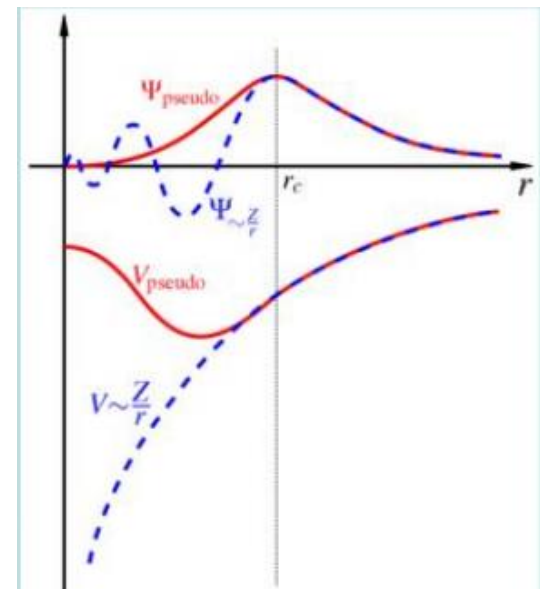
Pseudopotentials and planewaves

H-like AOs have STO functional form: exponential decay and discontinuity at nucleus



Essential to remove region of fast variation in AO, WF, ρ

Achieved through pseudopotentials
Not only core e but also valence e close to nucleus
(even H needs a pseudopot.)



Local orbitals vs planewaves - 1

Complementary features

Cost of the calculations

- Local orbitals: few functions, $O(10^3)$.
Expensive part is the calculation of integrals

$$\int dx_1 dx_2 \chi_a^*(x_1) \chi_b(x_1) r_{12}^{-1} \chi_b^*(x_2) \chi_a(x_2)$$

- Planewaves: many functions, $O(10^6)$.
Expensive part is the diagonalisation (at each k pt)

$$F(k)C(k) = S(k)C(k) \quad (k)$$

Numerical integration of solution in reciprocal space...

Local orbitals vs planewaves - 2

Which Hamiltonian?

- Local orbitals:
local nature enables truncation of sums
(distance or overlap between AOs)
- Planewaves:
truncations require localisation (Wannier fcts)

HF: 2e integrals (Coulomb, Exchange) run over 4 indices $\langle ij|kl \rangle$

DFT (local functionals): integrals run over 2 BS indices

Planewaves best suited for DFT (local functionals)

Local orbitals more natural choice for HF (including hybrid DFT)

Problem even more critical for post-HF techniques

Truncation of sums is imperative

Summary – a word of wisdom

When it comes to QM methods we are spoilt for choice

- Hamiltonians
- Basis set types
- Models, e.g. PBC vs (embedded) clusters

Each has advantages and disadvantages;

Best suited combinations: PW-local DFT, AO-wavefct

If we understand what they are we can exploit at best the capability of the techniques and at the lowest cost

When it comes to basis sets, we can test convergence

The best PW and AO result (for the same Hamiltonian) must converge to the same value

Some “black magic”: which BS size in AOs, pseudos in PW
PW more restrictive in the choice of Hamiltonian