Basis sets for SIESTA
I. Non-orthogonal representations and LCAO

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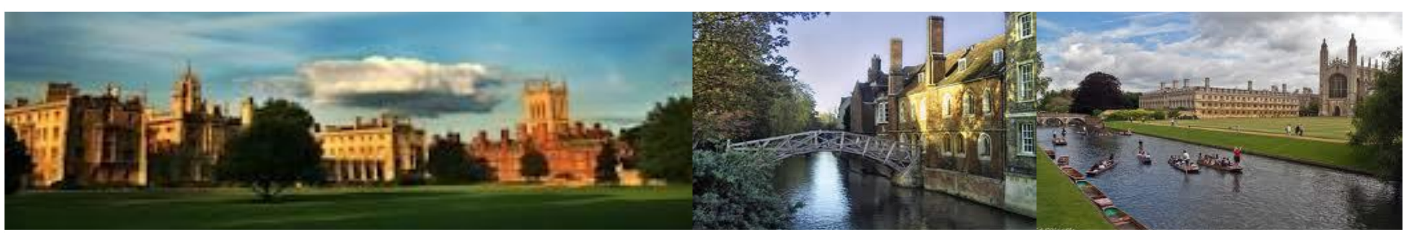

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BUT PRESENTING WORK OF MANY OTHERS!

Solving Kohn-Sham Hamiltonian using a finite non-orthogonal basis set

Kohn-Sham problem:

$$H|\psi_n\rangle = E_n|\psi_n\rangle$$

Expand in basis set:

$$|\psi\rangle = \sum_{\mu} |e_\mu\rangle\, C_\mu\,, \qquad \mu = 1, 2 \ldots \mathcal{N}$$

Basis states (orbitals):

$$\phi_\mu(\mathbf{r}) = \langle \mathbf{r}|e_\mu\rangle \qquad \{|e_\mu\rangle,\ \mu = 1 \ldots \mathcal{N}\}$$

Kohn-Sham equation becomes

Generalised Eigenvalue Problem

$$\sum_\nu H_{\mu\nu} C_\nu = E \sum_\nu S_{\mu\nu} C_\nu$$

General, including basis sets that are not orthonormal

$$H_{\mu\nu} = \langle e_\mu|H|e_\nu\rangle \text{ and } S_{\mu\nu} = \langle e_\mu|e_\nu\rangle$$

Solving Kohn-Sham Hamiltonian using a finite non-orthogonal basis set

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Expand in basis set: $$|\psi\rangle = \sum_\mu |e_\mu\rangle C_\mu\,, \qquad \mu = 1, 2 \ldots \mathcal{N}$$

Basis states (orbitals): $$\phi_\mu(\mathbf{r}) = \langle \mathbf{r}|e_\mu\rangle$$ $$\{|e_\mu\rangle,\ \mu = 1 \ldots \mathcal{N}\}$$

FINITE

Kohn-Sham equation becomes

Generalised Eigenvalue Problem

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HOW MANY?

General, including basis sets that are not orthonormal

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Density and finite basis set

$$n(\mathbf{r}) = \sum_{n}^{\text{occ}} |\psi_n(\mathbf{r})|^2 = \sum_{n}^{\text{occ}} \psi_n(\mathbf{r})\psi_n^*(\mathbf{r}) = \sum_{n}^{\text{occ}} \sum_{\mu,\nu} C_{\mu n}\phi_\mu(\mathbf{r})\, C_{\nu n}^*\phi_\nu^*(\mathbf{r})$$

$$= \sum_{\mu,\nu} \rho_{\mu\nu}\phi_\mu(\mathbf{r})\,\phi_\nu^*(\mathbf{r}) \quad \text{where} \quad \rho_{\mu\nu} \equiv \sum_{n}^{\text{occ}} C_{\mu n}C_{\nu n}^*$$

Density matrix

$$H_{\mu\nu} = \langle e_\mu | H | e_\nu \rangle \text{ and } S_{\mu\nu} = \langle e_\mu | e_\nu \rangle$$

Hamiltonian matrix and Overlap matrix

Non-orthogonal basis sets: Tensors
oblique axes (non-orthogonal but not moving)

Tensors, defining the dual basis $|e^\mu\rangle$ such that $\langle e^\mu|e_\nu\rangle = \langle e_\nu|e^\mu\rangle = \delta^\mu_\nu$

$$\sum_\mu |e_\mu\rangle\langle e^\mu| = \sum_\mu |e^\mu\rangle\langle e_\mu| = P_\Omega$$

Usual Schrödinger becomes

(in the natural representation)

$$H|\Psi\rangle = E|\Psi\rangle$$

$$H^\mu{}_\nu\,\psi^\nu = E\,\psi^\mu$$

All well-behaved tensors $\psi^\mu = \langle e^\mu|\psi\rangle \quad H^\mu{}_\nu = \langle e^\mu|H|e_\nu\rangle$

$$S_{\mu\nu} = \langle e_\mu|e_\nu\rangle \quad S^{\mu\nu} = \langle e^\mu|e^\nu\rangle \quad S^{\mu\lambda}S_{\lambda\nu} = \delta^\mu{}_\nu$$

$$S^{\mu\lambda}H_{\lambda\nu} = H^\mu{}_\nu$$

D. Vanderbilt and J. D. Joannopoulos, PRB 1980

L. E. Ballantine and M. Kolá, J Phys C 1986

E. Artacho and L. Miláns del Bosch, PRA 43 1991

M. Head-Gordon, P. E. Maslen, and C. A. White, JCP 1998

Evolving states in a moving basis

(e.g. when doing TDDFT and moving atoms)

The time evolving KS eq. becomes $$H|\psi\rangle = i\,\partial_t|\psi\rangle$$

$$\sum_{\nu}(H_{\mu\nu} - i\,D_{\mu\nu})C_{\nu} = i\sum_{\mu\nu} S_{\mu\nu}\,\partial_t C_{\nu}$$

$$D_{\mu\nu} = \langle e_{\mu}|\partial_t|e_{\nu}\rangle = \langle e_{\mu}|\partial_t e_{\nu}\rangle$$

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Set of states not a Hilbert space, but a curved manifold (a fibre bundle)

$$H^{\mu}{}_{\nu}\psi^{\nu} = i\,\eth_t\,\psi^{\mu}$$

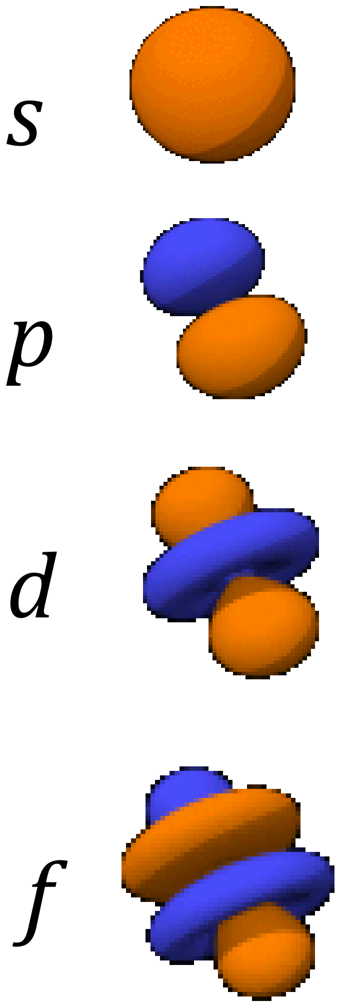
Covariant derivative:

$$\eth_t\psi^{\mu}{}_{n} = \partial_t\psi^{\mu}{}_{n} + D^{\mu}{}_{\nu t}\psi^{\nu}{}_{n}$$

Connection (as in Berry)

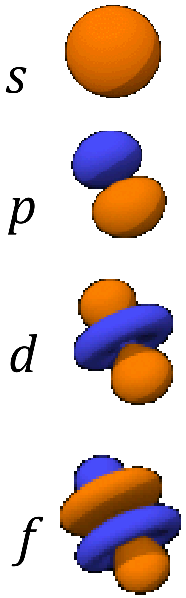
E Artacho & D D O'Regan, PRB 2017

Basis sets used in electronic structure

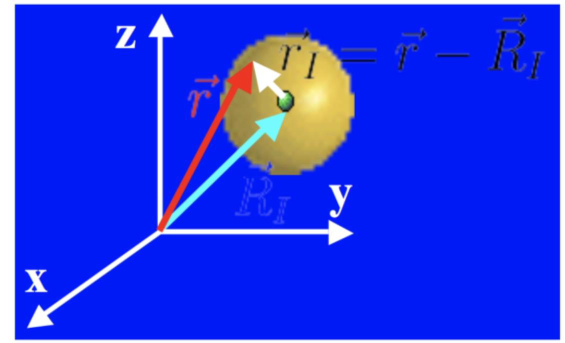


- Plane waves
- Atomic orbitals
    - Various kinds
- Many more:
    - Psinc's, blips
    - Wavelets
    - Bessel functions
    - Augmented plane waves
    - Muffin-tin orbitals
    - etc

Atomic orbitals (or atomic-like)



$$\phi_{Ilmn}(\mathbf{r_I}) = R_{Iln}(r)Y_{lm}(\hat{\mathbf{r}}_I)$$



ADVANTAGES

- Very efficient (number of basis functions needed is usually very small)
- Large reduction of CPU time and memory
- Direct physical/chemical interpretation (population analysis, projected density of states)
- Vacuum (almost) for free

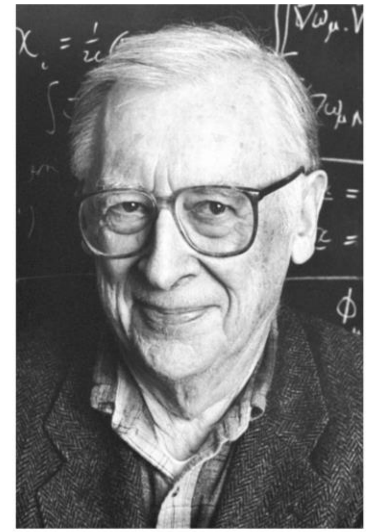
DISADVANTAGES

- No systematics for convergence (no unique way to enlarge the basis set)
- Human and computational effort needed for good basis set before facing a realistic project
- Depend on the atomic position (Pulay terms appearing in the forces)

LCAO basis functions: Radial shapes

- Atomic solutions. Actual atomic orbitals. Nodes inconvenient
- STO. Slater-type orbitals $R_{\text{STO}}(r) \sim r^l e^{-\alpha r}$
- GTO. Gaussians $R_{\text{GTO}}(r) \sim r^l e^{-\alpha r^2}$ $\longrightarrow$
  - wrong decay
  - convenient: integrals analytic
- CGTO. Contracted Gaussians

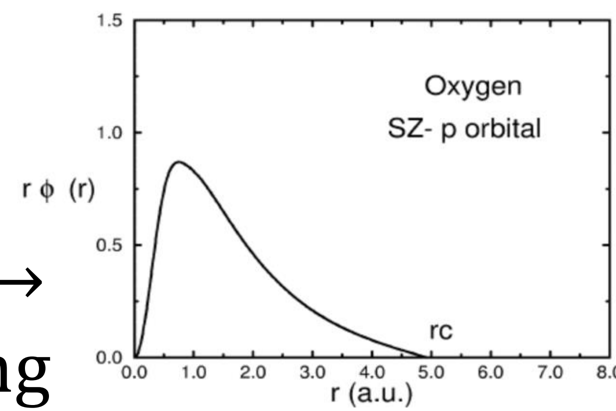
$$R(r) = \sum_i C_i r^l e^{-\alpha_i r^2}$$



John Pople

- Numerical. r-grid
  - DFT solutions of (pseudo) atoms
  - Finite support (strictly zero beyond r_c) $\rightarrow$

    $\Rightarrow$ Sparse matrices $\Rightarrow$ linear scaling



Constructing LCAO bases

- *Minimal basis*. Occupied or partly occupied l-shells of free atom
    - Also called single-ζ (SZ)
    - O: (core) $2s$, $2p_x$, $2p_y$, and $2p_z$
    - Fe: (core) $3d$ and $4s$
- *Multiple-ζ*. Radial flexibility
    - Double-ζ (DZ). 2 orbitals (different $R_l(r)$) for each valence SZ orbital
    - TZ, QZ etc.
- *Polarisation*. Angular flexibility. Add new shell with $l + 1$ w.r.t. valence
    - Add $3d$ shell to valence of C, Si, O, F, etc.
    - Add $4p$ and/or $4f$ shells to Fe valence (polarising $4s$ and/or $3d$)
- *Diffuse functions*. Add radial function on pre-existing valence shell, with longer tail than free atom

LCAO hierarchy of basis sizes

Standarised basis tiers

General procedure

- Start from SZ
- Every step: increase both ζ and polarisation by one

Resulting in

- Single-ζ (SZ) or minimal
- DZP: double-ζ polarised (extra l + 1 shell)
- TZDPP’: triple-ζ doubly polarised
  (two shells of l + 1, and one of l+2)
- QZPTPDP’P”, etc.

LCAO Accuracy

REMEMBER:

Quantum Chemistry theories such as Coupled Cluster CCSD(T) often quoted as

Accuracy Gold Standard in ab initio calculations

They are LCAO

You control the accuracy of the basis

Usual tradeoff accuracy/efficiency

Needs depend on

- System
- Property
- Problem

YOU are responsible of choice of

- DFT XC
- Pseudo
- Basis

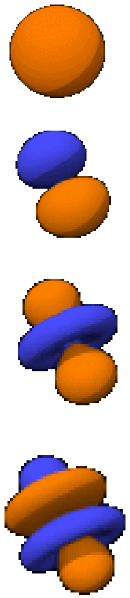
& convergence of technical parameters (r-grid, k-grid, etc)

Beware of statements such as “SIESTA is more efficient than …” or “SIESTA is less accurate than …”

Most times they refer to the chosen approximations (as chosen by the user!)

SIESTA basis sets

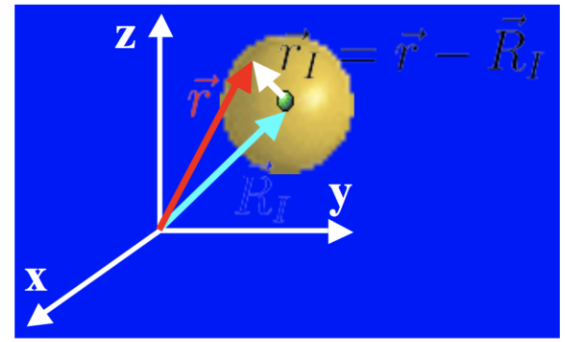
s
p
d
f



ONLY REQUIREMENTS:

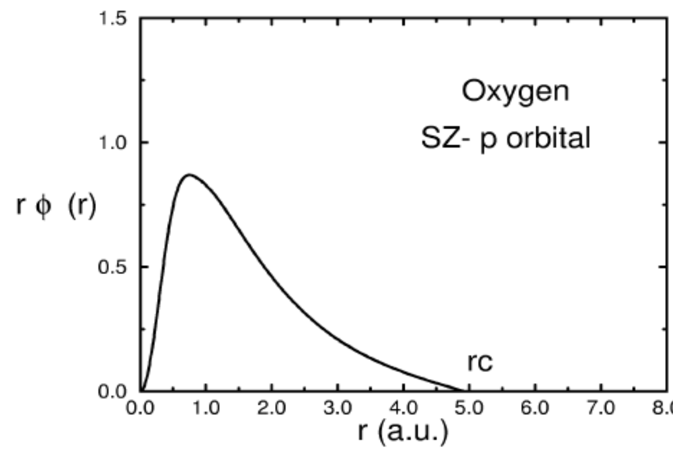
1. Of the general shape:

$$\phi_{Ilmn}(\mathbf{r_I}) = R_{Iln}(r)Y_{lm}(\hat{\mathbf{r}}_I)$$

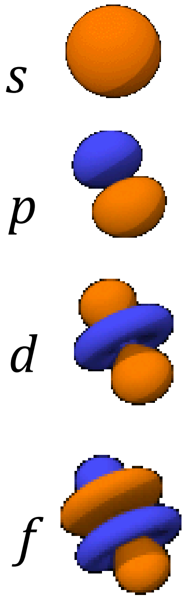


2. Of finite support:

Strictly zero beyond a cutoff radius r_c



SIESTA basis sets



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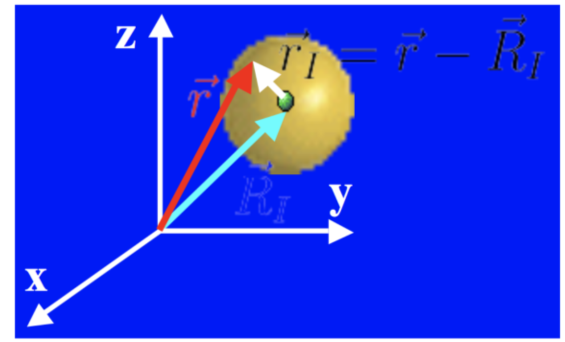

2. Of finite support:

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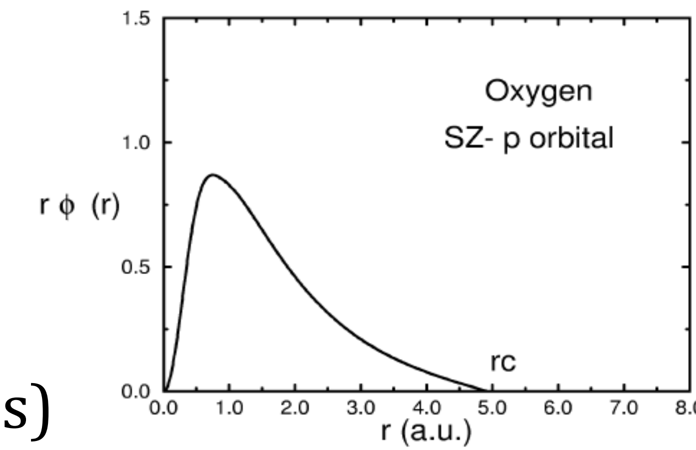
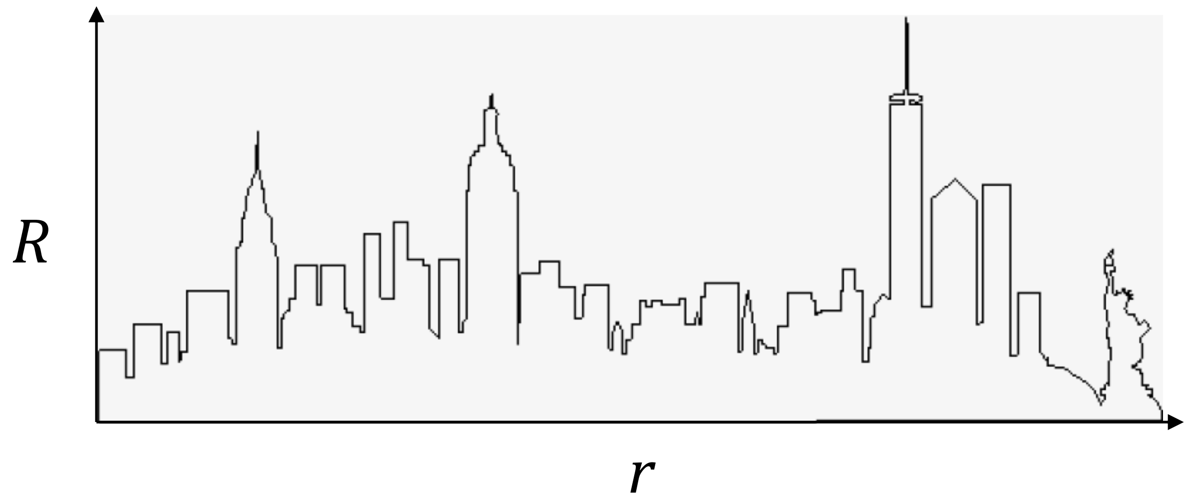
They can be:

- As many as you want (l-channels and ζ's)
- Of any (radial) shape
- Of any cutoff radius
- Centred anywhere (not necessarily on atoms)



You could even use



Just introduce a fine-enough numerical table with this radial dependence

(actually, not this one (a pity), it is not a single-valued function $R(r)$)

Concluding

- Finite basis sets transform Kohn-Sham problem to linear algebra (generalised eigenvalue) problem, amenable to linear algebra libraries (e.g. ScaLAPACK)
- Formalism for non-orthogonal bases (generalising Dirac's)
- Size of problem depends on how many basis functions are needed (diagonalization scales as N^3)
- Different kinds of basis sets (PWs, LCAO, and many others)
- LCAO:
  - Atomic-like functions (Radial * Spherical harmonics centred where wanted)
  - Radial-function kinds
  - Ways of increasing basis size for convergence
  - Systematics, convergence tiers
- SIESTA bases: Atomic-like and finite support as only requirements

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