SIESTA School 2025

Basis sets in SIESTA

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A quick refreshment of DFT

- **Kohn-Sham equations:**

$$\hat{H}_{\mathrm{KS}}\psi_j^{\mathrm{KS}}(\mathbf{r}) = \varepsilon_j\psi_j^{\mathrm{KS}}(\mathbf{r})$$

$$\hat{H}_{\mathrm{KS}} = -\frac{1}{2}\nabla^2 + \hat{V}_{\mathrm{KS}}(\mathbf{r})$$

$$\hat{V}_{\mathrm{KS}}(\mathbf{r}) = \hat{V}_{ext}(\mathbf{r}) + \hat{V}_{Hartree}(\mathbf{r}) + \hat{V}_{xc}(\mathbf{r})$$

$$\hat{V}_{ext}(\mathbf{r}) \Leftrightarrow n(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^N \left|\psi_i^{\mathrm{KS}}(\mathbf{r})\right|^2$$

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- **Basis expansion:**

Basis functions

$$|\psi_i^{\mathrm{KS}}(\mathbf{r})\rangle = \sum_{\mu=1}^{M} c_{i,\mu}|\mu\rangle$$

Generalized eigenvalue problem:

$$H_{\mu\nu}C_{j\nu} = \varepsilon_j S_{\mu\nu}C_{j\nu}$$

Hamiltonian matrix:

$$H_{\mu\nu} = \langle\mu|\hat{H}|\nu\rangle$$

Overlap matrix:

$$S_{\mu\nu} = \langle\mu|\nu\rangle$$

Completely general
(even for non-orthogonal basis sets)

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A quick refreshment of DFT

$$\hat{H}_{\mathrm{KS}}\psi_j^{\mathrm{KS}}(\mathbf{r}) = \varepsilon_j\psi_j^{\mathrm{KS}}(\mathbf{r})$$

- **Particle density:**

$$n(\mathbf{r}) = \sum_i^N \left|\psi_i^{\mathrm{KS}}(\mathbf{r})\right|^2$$

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$$n(\mathbf{r}) = \sum_i^N \left|\psi_i^{\mathrm{KS}}(\mathbf{r})\right|^2 =$$

$$|\psi_i^{\mathrm{KS}}(\mathbf{r})\rangle = \sum_{\mu=1}^{M} c_{i,\mu}|\mu\rangle$$

$$\phi_\mu(\mathbf{r}) = \langle\mathbf{r}|\mu\rangle$$

$$= \sum_i^N \sum_{\mu\nu}^M c_{i,\mu}c_{i,\nu}^*\phi_\mu(\mathbf{r})\phi_\nu^*(\mathbf{r}) =$$

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$$\rho_{\mu\nu} \equiv \sum_i^N c_{i,\mu} c_{i,\nu}^*$$

$$= \sum_{\mu\nu}^M \rho_{\mu\nu} \phi_\mu(\mathbf{r}) \phi_\nu^*(\mathbf{r})$$

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Density matrix!

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Basis sets

$$|\psi_i^{\mathrm{KS}}(\mathbf{r})\rangle = \sum_{\mu=1}^{M} c_{i,\mu}|\mu\rangle$$

- **Periodic boundary conditions (PBC):**

We can use the Bloch theorem

$$|\mu\rangle \Rightarrow |\mu\boldsymbol{k}\rangle = \frac{1}{\sqrt{N}}\sum_{\mu} e^{-i\boldsymbol{k}\mathbf{R}}\,|\mu\mathbf{R}\rangle \quad \longrightarrow \quad |\mu\rangle \Rightarrow |n\boldsymbol{k}\rangle = \frac{1}{\sqrt{N}}\sum_{\mu,\mathbf{R}} c_{n,\mu}(\boldsymbol{k})e^{-i\boldsymbol{k}\mathbf{R}}\,|\mu\mathbf{R}\rangle$$

Generalized eigenvalue problem:

$$H_{\mu\nu}(\boldsymbol{k})C_{j\nu}(\boldsymbol{k}) = \varepsilon_{j,\boldsymbol{k}}S_{\mu\nu}(\boldsymbol{k})C_{j\nu}(\boldsymbol{k})$$

Hamiltonian matrix: $H_{\mu\nu}(\boldsymbol{k}) = \langle\mu\boldsymbol{k}|\hat{H}|\nu\boldsymbol{k}\rangle = \sum_{\mathbf{R}} e^{-i\boldsymbol{k}\mathbf{R}}\langle\mu\mathbf{0}|\hat{H}|\nu\mathbf{R}\rangle$

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Basis functions: Types

- Representation of the Hilbert space for the electronic wavefunctions
- There are many types:
    - Planewaves
    - Atomic orbitals
    - Wavelets
    - Bessel functions
    - Augmented plane waves
    - Muffin-tin orbitals
    - …

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Basis functions: Plane waves (PW)

- Advantages:
  - Good for writing equations with PBC
  - Expressions for H are simple (Fast Fourier Transform)
  - Convergence: Systematic and complete
  - Orthogonal
  - Spatially unbiased

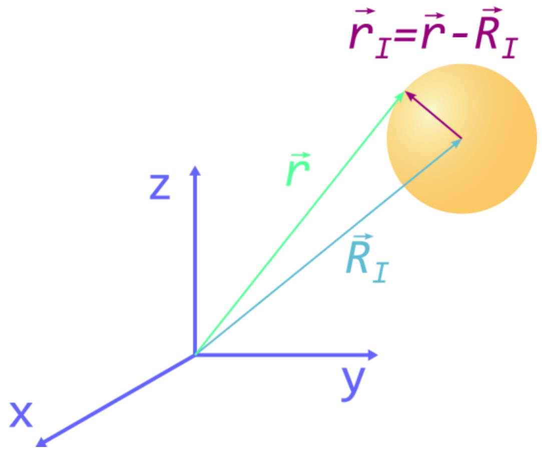
- Disadvantages:
  - Vacuum is expensive! (Costs as much as matter).
  - We need a large number of PW per electron
  - Compact orbitals are harder to describe
  - Localization ideas are not easy to implement

Basis functions: Atomic orbitals

Atomic orbitals

$$|\psi_i^{\mathrm{KS}}(\mathbf{r})\rangle = \sum_{\mu=1}^{M} c_{i,\mu}|\mu\rangle$$

$$\langle\mathbf{r}|\mu\rangle = \phi_\mu(\mathbf{r}) \rightarrow \phi_\mu(\mathbf{r}-\mathbf{R}_I)$$



Atomic orbitals

LCAO methods

$$|\psi_i^{\mathrm{KS}}(\mathbf{r})\rangle = \sum_{\mu=1}^{M} c_{i,\mu} |\mu\rangle$$

Orbitals close to the solutions of the atomic problem are good approximations

$$\phi_\mu(\mathbf{r}-\mathbf{R}_I) \equiv \phi_{Iplm}(\mathbf{r}_I) = R_{Ipl}\,(\mathrm{r})\,Y_{lm}\,(\mathbf{r}_I)$$

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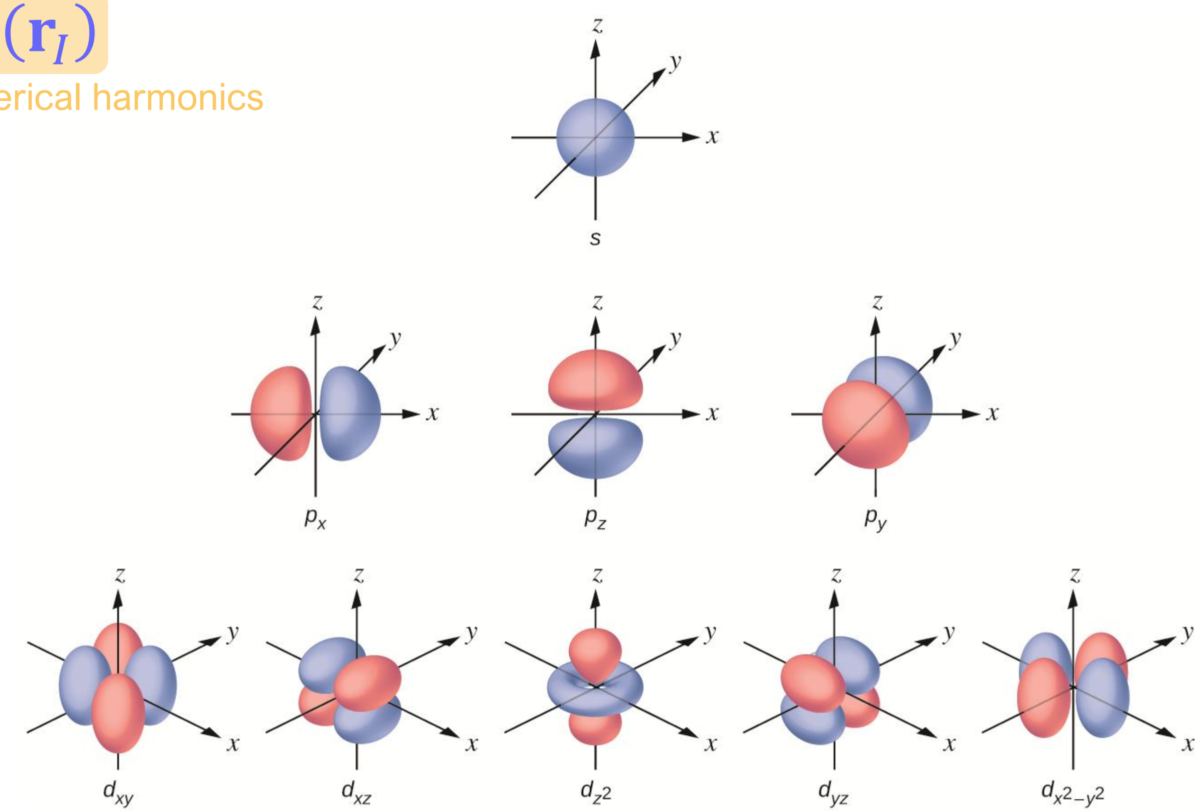

Taken from: https://chem.libretexts.org/

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I → Atom index

l → Angular momentum

m → Magnetic quantum number

p → Multiple orbitals for the same lm

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Very common (tradition) from quantum chemistry methods:

- Slater-type orbitals (STO)
- Gaussian-type orbitals (GTO)
- Contracted Gaussian-type orbitals
- Numerical real-space grid

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Atomic orbitals

- Advantages:
  - Very efficient in terms of number of orbitals per electrons.
  - Very well suited to describe localization.
  - Large reduction in CPU and memory costs.
  - No need for periodicity.
  - Vacuum is almost free.
  - Chemical information (charge population, projected density of states, etc).

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  - Chemical information (charge population, projected density of states, etc).

- Disadvantages:
  - Lack of systematics for convergence.
  - Require human and computational effort to get a good basis set before use.
  - Spatially biased, since they are optimal for an atomic problem: Basis Set Superposition Error.
  - Orbitals move with atoms, which brings extra terms in forces (Pulay corrections).
  - Calculation of Hamiltonian matrix elements can be quite complicated (and expensive).

Atomic orbitals

$$\phi_\mu(\mathbf{r}-\mathbf{R}_I) \equiv \phi_{Iplm}(\mathbf{r}_I) = \boxed{R_{Ipl}\,(\mathrm{r})}\,\boxed{Y_{lm}\,(\mathbf{r}_I)}$$

Radial flexibility

Spherical harmonics

- Mininal basis set (single-ζ or SZ)
  - One single radial function per angular momentum shell occupied in the free atom
- Multiple-ζ
  - Add more than one radial function with the same angular momentum.
  - double-ζ (DZ), triple-ζ (TZ), cuadruple-ζ (QZ), …
- Diffuse functions
  - Add radial function on pre-existing valence shell, with longer tail than free atom

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Atomic orbitals

$$\phi_\mu(\mathbf{r}-\mathbf{R}_I) \equiv \phi_{Iplm}(\mathbf{r}_I) = \underbrace{R_{Ipl}\,(\mathrm{r})}_{\text{Radial flexibility}}\,\underbrace{Y_{lm}\,(\mathbf{r}_I)}_{\text{Angular flexibility}}$$

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  - One single radial function per angular momentum shell occupied in the free atom
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  - double-ζ (DZ), triple-ζ (TZ), cuadruple-ζ (QZ), …
- Diffuse functions
  - Add radial function on pre-existing valence shell, with longer tail than free atom
- Polarization orbitals
  - Add new shells with larger value of "l"
    - *d*-orbitals for C, N, O, …
    - *f*-orbitals for Mn, Fe, …

Basis sets: Hierarchy

- Generating basis sets for a calculation:
  1. Start from SZ
  2. Increase both the number of ζ and polarization functions one by one

  General philosophy: Larger number of orbitals → Better quality of basis set.

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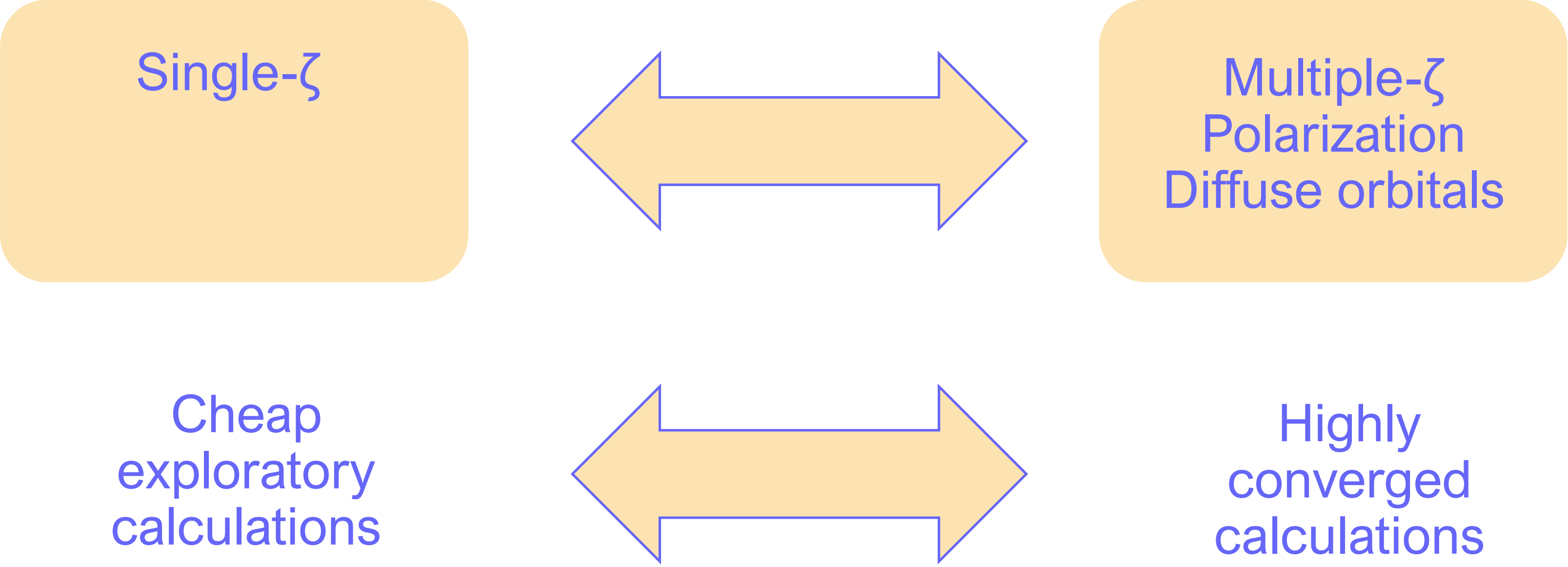


Single-ζ

Multiple-ζ
Polarization
Diffuse orbitals

Cheap
exploratory
calculations

Highly
converged
calculations

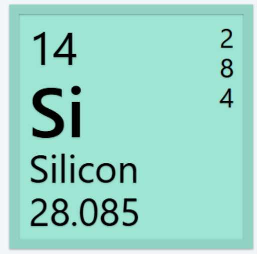
Basis sets: Examples

14 2 8 4
Si
Silicon
28.085

Valence electrons	SZ	
	#orbitals	symmetry
$3s^2\ 3p^2$	1	s
	1	p_x
	1	p_y
	1	p_z

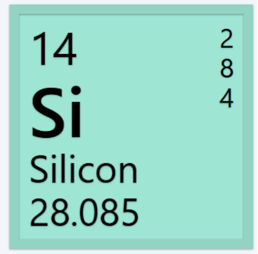
Total number of orbitals: 4

Basis sets: Examples



Valence electrons	SZ		DZ	
	#orbitals	symmetry	#orbitals	symmetry
$3s^2\ 3p^2$	1	s	2	s
	1	p_x	2	p_x
	1	p_y	2	p_y
	1	p_z	2	p_z
Total number of orbitals:	4		8	

Basis sets: Examples



Valence electrons	SZ		DZ		Polarization (P)	
	#orbitals	symmetry	#orbitals	symmetry	#orbitals	symmetry
$3s^2\ 3p^2$	1	s	2	s	1	d_{xy}
	1	p_x	2	p_x	1	d_{yz}
	1	p_y	2	p_y	1	d_{zx}
	1	p_z	2	p_z	1	$d_{x^2-y^2}$
					1	$d_{3z^2-r^2}$
Total number of orbitals:	4		8		13 DZ+P = DZP	

Basis sets: Examples

1	s
1	d_{xy}
1	d_{yz}
1	d_{zx}
1	$d_{x^2-y^2}$
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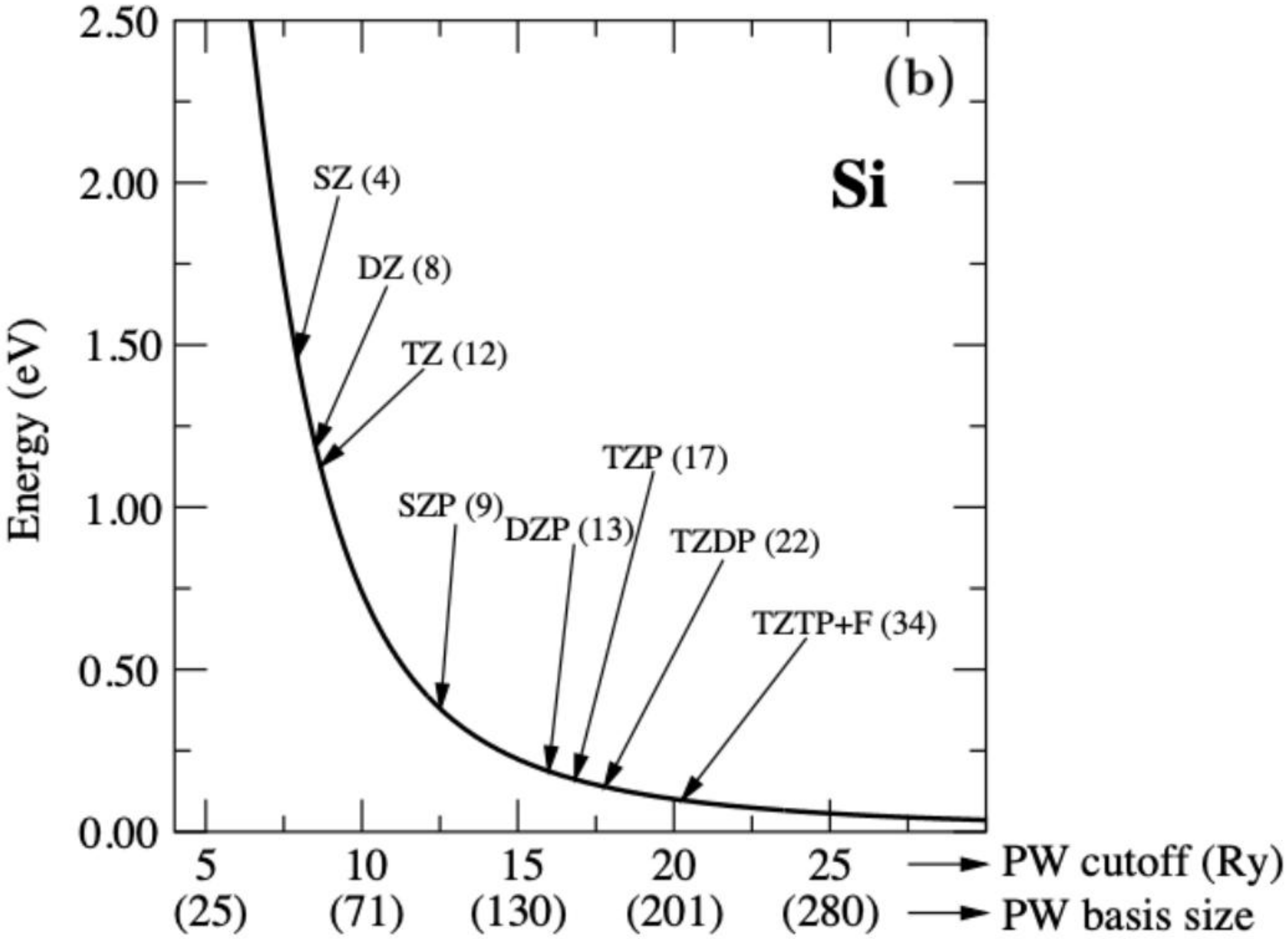
Total number of orbitals:	4		8		13 DZ+P = DZP	

26 2 8 14 2
Fe
Iron
55.845

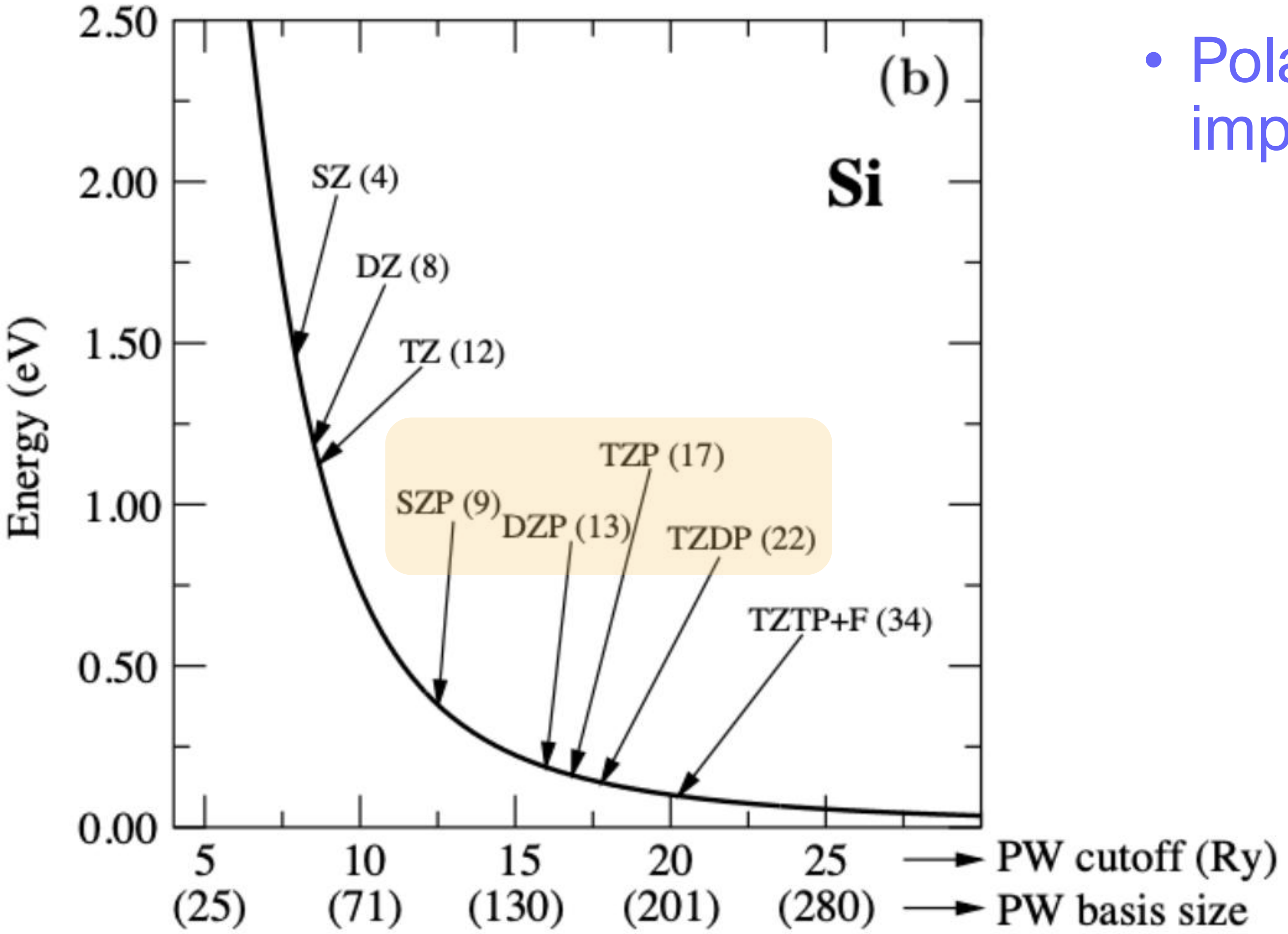
Valence electrons	SZ		DZ		Polarization (P)	
	#orbitals	symmetry	#orbitals	symmetry	#orbitals	symmetry
$4s^2\ 3d^6$	1	s	1	s	1	p_x
	1	d_{xy}	1	d_{xy}	1	p_y
	1	d_{yz}	1	d_{yz}	1	p_z
	1	d_{zx}	1	d_{zx}		
	1	$d_{x^2-y^2}$	1	$d_{x^2-y^2}$		
	1	$d_{3z^2-r^2}$	1	$d_{3z^2-r^2}$		
Total number of orbitals:	6		12		15 DZ+P = DZP	

Basis sets: Convergence



Phys. Rev. B **64**, 235111 (2001)

Basis sets: Convergence



- Polarization orbitals are important for convergence.

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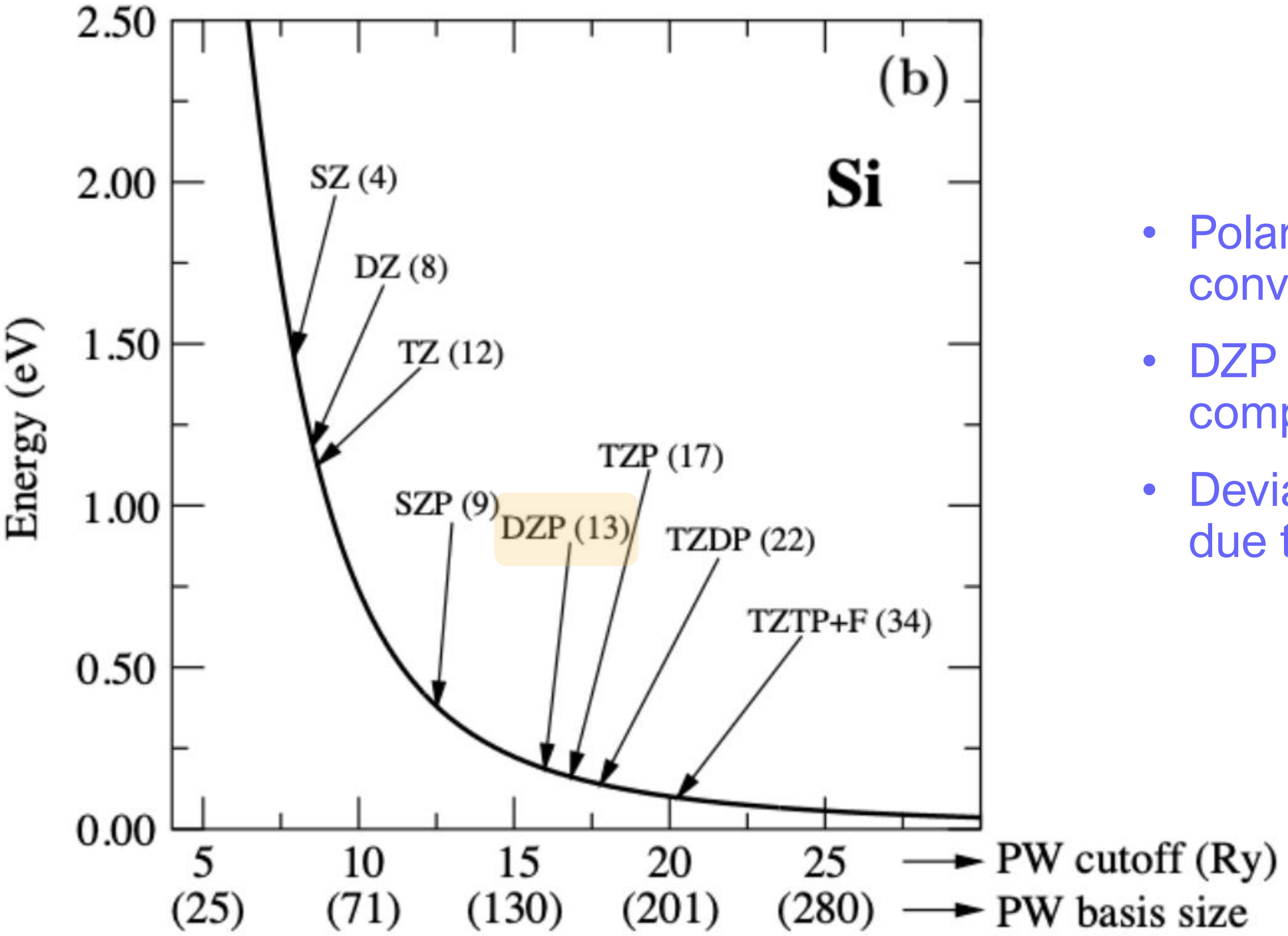
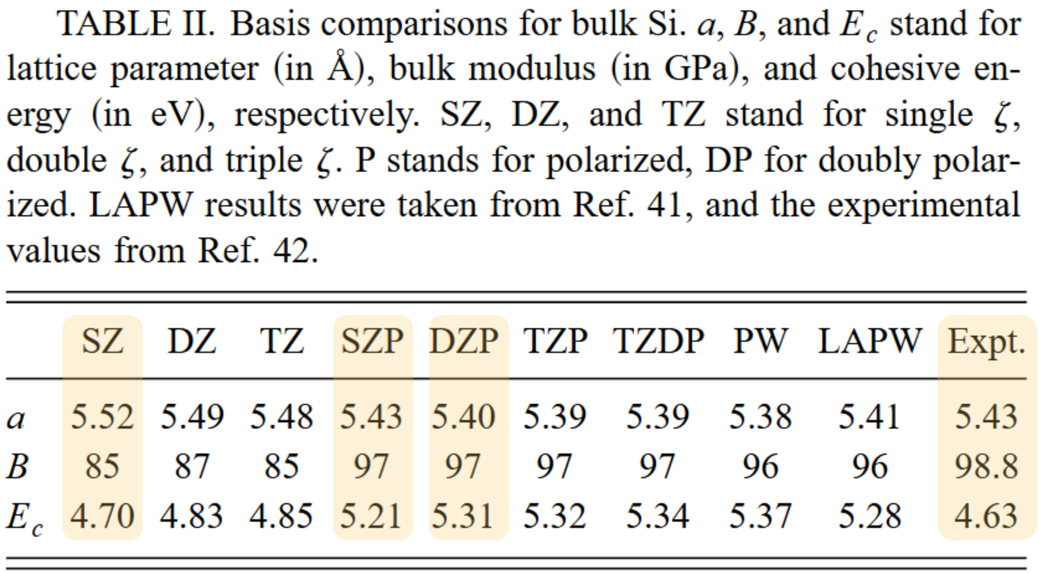
Basis sets: Convergence



Phys. Rev. B **64**, 235111 (2001)

- Polarization orbitals are important for convergence.
- DZP basis is usually “good enough” as compared to converged PW calculations.
- Deviations are comparable to differences due to pseudopotentials or XC functionals

Basis sets: Convergence



Phys. Rev. B **64**, 235111 (2001)

TABLE II. Basis comparisons for bulk Si. a, B, and E_c stand for lattice parameter (in Å), bulk modulus (in GPa), and cohesive energy (in eV), respectively. SZ, DZ, and TZ stand for single ζ, double ζ, and triple ζ. P stands for polarized, DP for doubly polarized. LAPW results were taken from Ref. 41, and the experimental values from Ref. 42.

	SZ	DZ	TZ	SZP	DZP	TZP	TZDP	PW	LAPW	Expt.
a	5.52	5.49	5.48	5.43	5.40	5.39	5.39	5.38	5.41	5.43
B	85	87	85	97	97	97	97	96	96	98.8
E_c	4.70	4.83	4.85	5.21	5.31	5.32	5.34	5.37	5.28	4.63

- Polarization orbitals are important for convergence.
- DZP basis is usually “good enough” as compared to converged PW calculations.
- Deviations are comparable to differences due to pseudopotentials or XC functionals

WARNING!! Basis can be optimized to get better agreement with experiments. That doesn’t necessarily mean the basis set is better. There are other approximations implied (e.g. the xc functional) that could be responsible for disagreements between calculations and experiments!!

Atomic orbitals: SIESTA

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$$\phi_{Iplm}(\mathbf{r}_I) = R_{Ipl}\,(\mathrm{r})\,Y_{lm}\,(\mathbf{r}_I)$$

- Linear combination of numerical pseudo atomic orbitals (PAO)
- Strictly localized: Zero beyond a certain radius from the nucleus: The cutoff radii (r_c)

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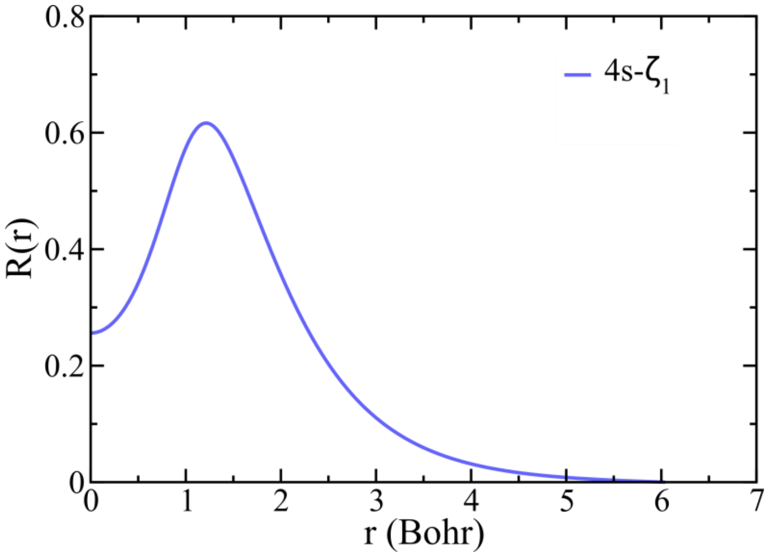

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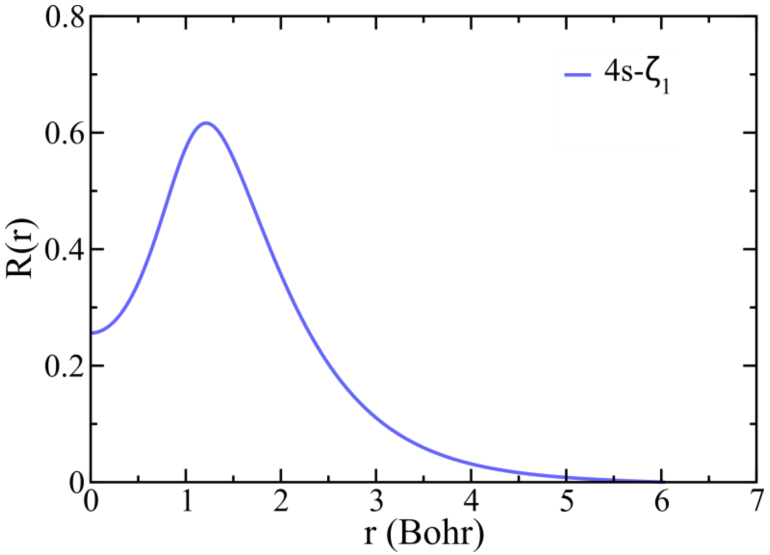
- Linear combination of numerical pseudo atomic orbitals (PAO)
- Strictly localized: Zero beyond a certain radius: The cutoff radius (r_c)
  - As many l and zetas (ζ) that you want
  - Any (radial) shape
  - As long as you want: r_c
  - Any center (not restricted to atom's position)
  - Numerical pseudo-atomic orbitals (PAO)



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Atomic orbitals: SIESTA

$$\phi_{Iplm}(\mathbf{r}_I) = \boxed{R_{Ipl}(\mathrm{r})}\, Y_{lm}(\mathbf{r}_I)$$

$R_{Ipl}(\mathrm{r})$ is automatically generated by SIESTA

- Based on finite-range pseudo-atomic orbitals [FIREBALLS: Sankey & Niklewski, Phys. Rev. B **40**, 3979 (1989)]
- Numerical solution of a pseudoatom + some "modifications"
- Depends on parameters that need to be defined by the user
- Quite tunable
- Various levels of automatism, and predefinition of default values for parameters

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- Solution of a Kohn-Sham DFT calculation of a (isolated) pseudo-atom under an added confinement potential

$$\left(-\frac{1}{2r}\frac{d^2}{dr^2}r + \frac{l(l+1)}{2r^2} + V_l(r)\right)R_l(n) = (\varepsilon_l + \delta\varepsilon_l)R_l(r)$$

Radial equation

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Radial equation

Energy shift:

Single parameter to choose r_c

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Radial equation

Energy shift:

Single parameter to choose r_c

The larger the Energy Shift, the shorter the r_c

Phys. Stat. Solidi (b) **215**, 809 (1999)

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$$\phi_{Iplm}(\mathbf{r}_I) = \boxed{R_{Ipl}\,(\mathrm{r})}\, Y_{lm}\,(\mathbf{r}_I)$$

First-ζ

1. **Hard wall potential**

$$\begin{cases} V(r < a) = 0 \\ V(r \geq a) = \infty \end{cases}$$

- Orbitals with discontinuous first derivates at r_c

2. **Soft confinement potential**

$$V(r) = V_0 \frac{e^{-\frac{r_c - r_i}{r - r_i}}}{r_c - r}$$

- Orbitals with continuous derivates
- Strictly localized (zero at r_c)
- Two parameters to optimize

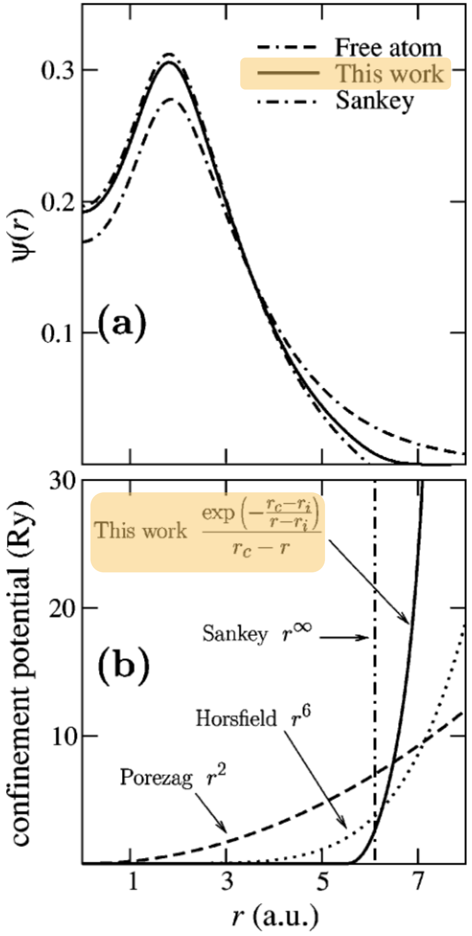


FIG. 1. Shape of the 3*s* orbital of Mg in MgO for the different confinement schemes (a) and corresponding potentials (b).

Phys. Rev. B **64**, 235111 (2001)

Atomic orbitals: SIESTA

$$\phi_{Iplm}(\mathbf{r}_I) = R_{Ipl}(r)\, Y_{lm}(\mathbf{r}_I)$$

Multiple-ζ

Atomic orbitals: SIESTA

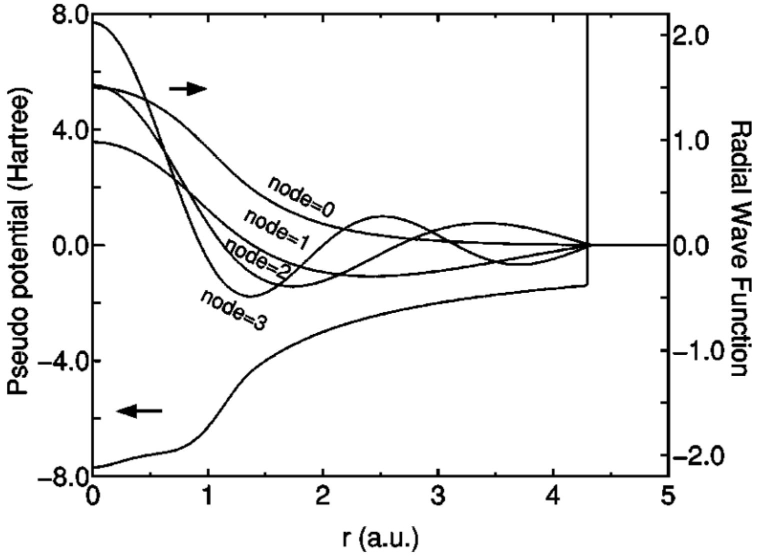
$$\phi_{Iplm}(\mathbf{r}_I) = R_{Ipl}(\mathrm{r})\, Y_{lm}(\mathbf{r}_I)$$

Multiple-ζ

1. **Pseudoatom-wavefunctions with increasing number of nodes:**
   (excited states of the confined pseudo-atom).
   - ✓ Orthogonality
   - ✓ Asymptotically complete (within sphere)

   - × Unbound excited states of pseudos
   - × Efficiency requires longer cutoff radius

Phys. Rev. B **69**, 195113 (2004)



Atomic orbitals: SIESTA

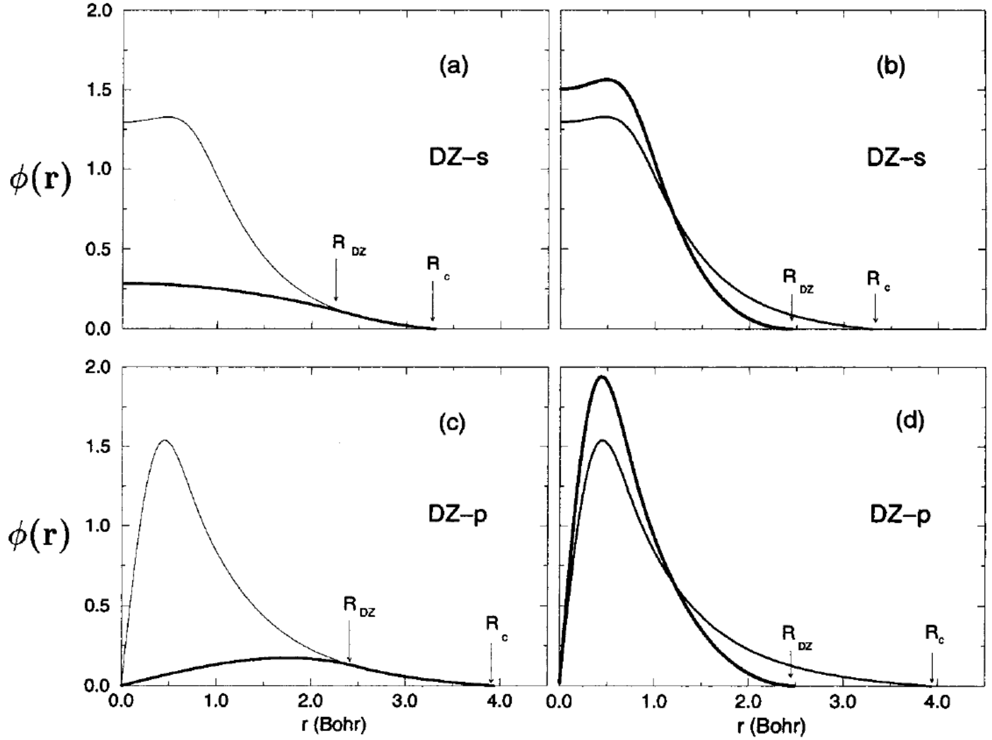
$$\phi_{Iplm}(\mathbf{r}_I) = R_{Ipl}(\mathrm{r})\, Y_{lm}(\mathbf{r}_I)$$

Multiple-ζ

2. Split-valence method:

$$\begin{cases} \chi_l^{2\zeta}(r) = r^l(a_l - b_i)r^2 \; if\; r < r_l^s \\ \chi_l^{2\zeta}(r) = \chi_l^{1\zeta}(r) \qquad if\; r \geq r_l^s \end{cases}$$

- Choose r_l^s and continue smoothly towards the origin as $r^l(a_l - b_i)r^2$
- Two parameters: (a and b): the new orbitals and its first derivates must be continuous at r_l^s
- The second-ζ is the (normalized) difference between the first-ζ and the function above
- r_l^s is controlled with `PAO.Splitnorm` (default = 0.15)



Phys. Stat. Solidi (b) **215**, 809 (1999)

siesta

Atomic orbitals: SIESTA

$$\phi_{Iplm}(\mathbf{r}_I) = R_{Ipl}(\mathrm{r})\, Y_{lm}(\mathbf{r}_I)$$

Generation of the polarization orbitals

Shell with a higher angular momentum to polarize the most extended valence orbital (l) to give angular freedom to the valence electrons

Atomic orbitals: SIESTA

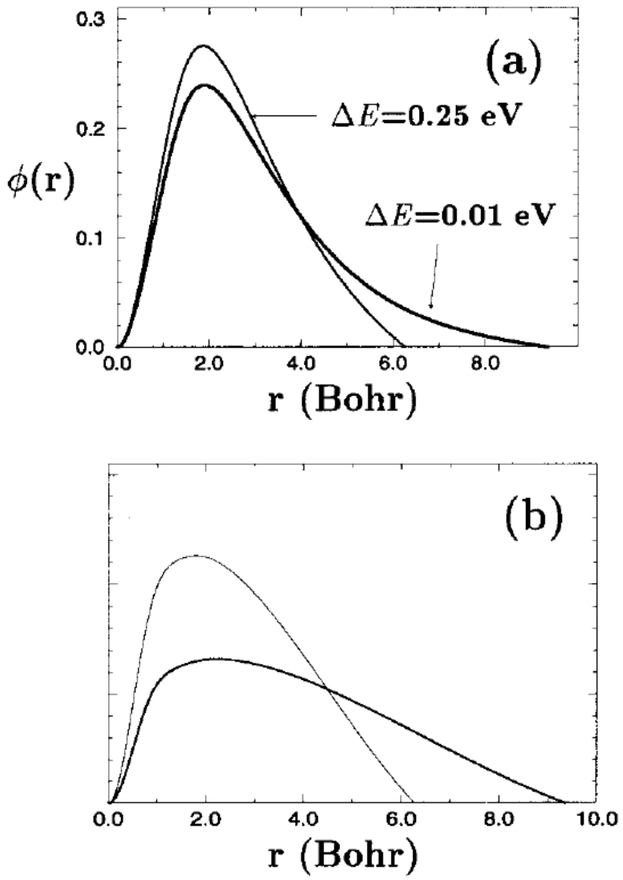
$$\phi_{Iplm}(\mathbf{r}_I) = R_{Ipl}(\mathrm{r})\, Y_{lm}(\mathbf{r}_I)$$

Generation of the polarization orbitals

1. **Perturbative polarization**
   - Free pseudo atom valence orbitals under an external electric field
   - $l+1$ orbitals with the same range of the unperturbed orbitals

2. **Atomic polarization**
   - Solve the Schrödinger equation for a free pseudo atom with higher angular momentum
   - Usually unbound: requires short cutoffs

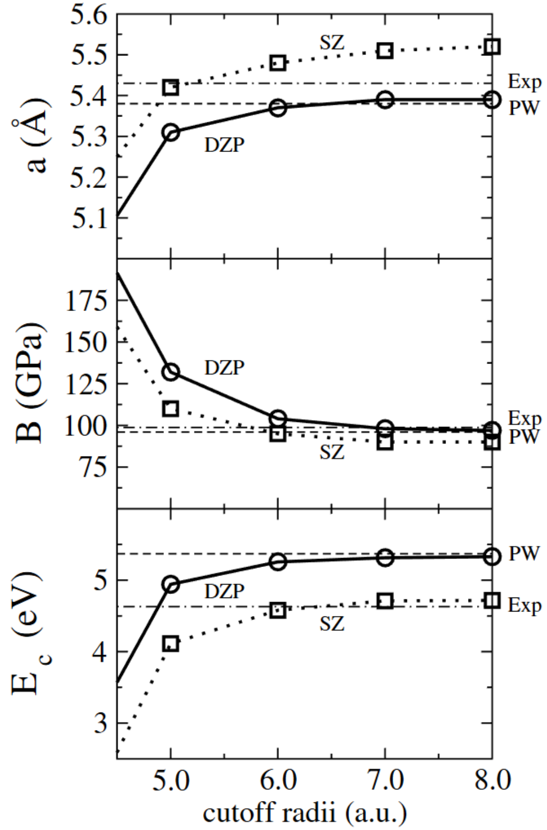
Polarization *d* orbitals for silicon



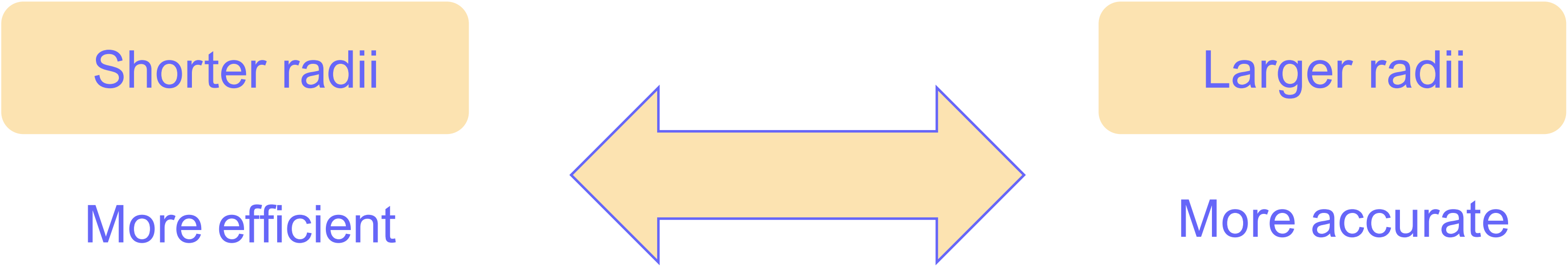
Phys. Stat. Solidi (b) **215**, 809 (1999)

Atomic orbitals: SIESTA

Convergence with the cutoff radius



J. Phys.: Condens. Matter **14**, 2745 (2002)



Shorter radii

More efficient

Larger radii

More accurate

WARNING!!

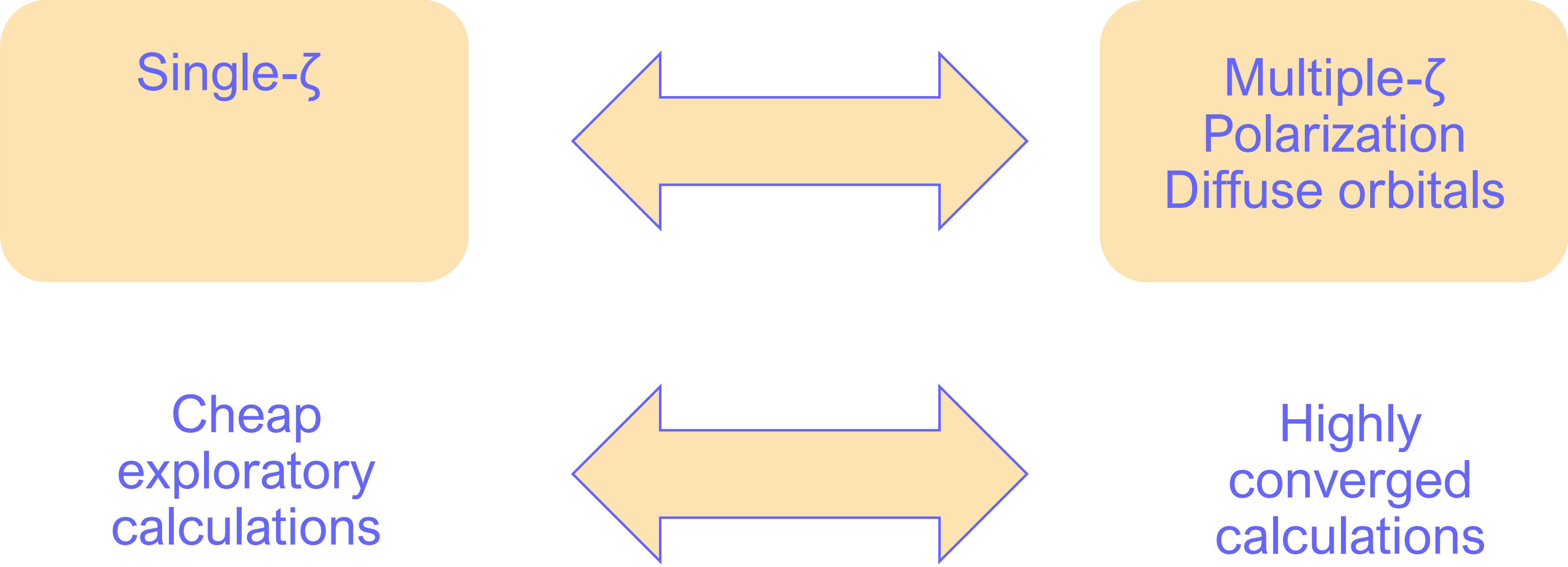
Basis can be optimized to get better agreement with experiments. That doesn't necessarily mean the basis set is better. There are other approximations implied (e.g. the XC functional) that could be responsible for disagreements between calculations and experiments!!

Small recap

Small recap

- Generating basis sets for a calculation:
  1. Start from SZ
  2. Increase both the number of ζ and polarization functions one by one

  General philosophy: Larger number of orbitals → Better quality of basis set.


Single-ζ

Multiple-ζ
Polarization
Diffuse orbitals

Cheap
exploratory
calculations

Highly
converged
calculations

Small recap

- Generating basis sets for a calculation:
  1. Start from SZ
  2. Increase both the number of ζ and polarization functions one by one

  General philosophy: Larger number of orbitals → Better quality of basis set.

- In SIESTA
  - ✓ Multiple options to generate basis sets
  - ✓ Hierarchical structure
  - ✓ Decent enough default basis sets (even more for versions > 5.0)

- Warning 1: Optimal orbitals are environment dependent!!!

- Warning 2: Basis can be optimized to get better agreement with experiments.
  That doesn't necessarily mean the basis set is better!!

General advice

- Tests your basis set before doing serious calculations
  - Although the default basis is usually a good starting point, it is important that you verify it is appropriate for your system.
    - (C orbitals in diamond are not necessarily good for molecular CO_2, or graphene)
  - If going to calculate for months or years, it is a good idea to spend a few days trying out bases and testing parameters is definitely worth it!
  - Sometimes people can share bases in communities, the SIESTA mailing list, or third parties.

- Warning 1: Optimal orbitals are environment dependent!!!

- Warning 2: Basis can be optimized to get better agreement with experiments. That doesn't necessarily mean the basis set is better!!

Practical stuff

Practical stuff

Basic way to input the basis set:

	FDF Flags	Default	Slightly better
Basis size:	PAO.BasisSize	DZP	
Range of first ζ:	PAO.EnergyShift	0.01 Ry	3-5 mRy
Second ζ:	PAO.BasisType	Split	
Range of second:	PAO.SplitNorm	0.15	
Confinement potential:	PAO.SoftDefault	True	
	PAO.SoftInnerRadius	0.9	
Fictitious pressure	BasisPressure	0.2 GPa	

Practical stuff

Advanced way to input the basis set:

```
%block PAO.BasisSize
   Si    DZ
   H     SZP
   O     DZP
%endblock PAO.BasisSize
```

Practical stuff

Advanced way to input the basis set:

```
%block PAO.BasisSize
   Si   DZ
   H    SZP
   O    DZP
%endblock PAO.BasisSize
```

```
%block PAO.Basis
  O 2
  n=2   0   2  E  50. 2.5
    0.0   0.0
    1.0   1.0
  n=2   1   2  P  1
    0.0   0.0
    1.0   1.0
%endblock PAO.Basis
```

`% Species | Number of orbitals`

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Practical stuff

Advanced way to input the basis set:

```
%block PAO.BasisSize
   Si    DZ
   H     SZP
   O     DZP
%endblock PAO.BasisSize
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  O 2
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    1.0   1.0
  n=2   1   2  P  1
    0.0   0.0
    1.0   1.0
%endblock PAO.Basis
```

```
% Species | Number of orbitals
% principal quatum number | angular momentum | number of ζ
```

Practical stuff

Advanced way to input the basis set:

```
%block PAO.BasisSize
   Si   DZ
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   O    DZP
%endblock PAO.BasisSize
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```
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    1.0   1.0
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    1.0   1.0
%endblock PAO.Basis
```

```
% Species | Number of orbitals
% principal quatum number | angular momentum | number of ζ
% type of confinement| parameters for the confinement potential
```

Practical stuff

Advanced way to input the basis set:

```
%block PAO.BasisSize
   Si   DZ
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```

```
%block PAO.Basis
  O 2
  n=2   0   2  E  50. 2.5
    0.0   0.0
    1.0   1.0
  n=2   1   2  P  1
    0.0   0.0
    1.0   1.0
%endblock PAO.Basis
```

```
% Species | Number of orbitals
% principal quatum number | angular momentum | number of ζ
% type of confinement| parameters for the confinement potential
% cutoff radius first-ζ| matching radius second-ζ
```

Practical stuff

Advanced way to input the basis set:

```
%block PAO.BasisSize
   Si   DZ
   H    SZP
   O    DZP
%endblock PAO.BasisSize
```

```
%block PAO.Basis
 O 2
 n=2   0   2  E  50. 2.5
     0.0   0.0
     1.0   1.0
 n=2   1   2  P  1
     0.0   0.0
     1.0   1.0
%endblock PAO.Basis
```

```
% Species | Number of orbitals
% principal quatum number | angular momentum | number of ζ
% type of confinement| parameters for the confinement potential
% cutoff radius first-ζ| matching radius second-ζ
% polarization orbitals | number of ζ for polarization
```

Practical stuff

Advanced way to input the basis set:

```
%block PAO.BasisSize
   Si   DZ
   H    SZP
   O    DZP
%endblock PAO.BasisSize
```

```
%block PAO.Basis
 O 2
 n=2   0   2  E  50. 2.5
   0.0   0.0
   1.0   1.0
 n=2   1   2  P  1
   0.0   0.0
   1.0   1.0
%endblock PAO.Basis
```

```
%block PAO.Basis
 O 3
 n=2   0   2
   0.0   0.0
   1.0   1.0
 n=2   1   2
   0.0   0.0
   1.0   1.0
 n=3   2   1
   0.0
   1.0
%endblock PAO.Basis
```

`% polarization orbitals | number of ζ for polarization`

Hands-on session:
Basis sets optimization

Problems…

Problems…

The VOID
(vacuum)

Problems… Localization is a double-edged sword

- Advantages:
  - Very efficient in terms of number of orbitals per electrons.
  - Very well suited to describe localization.
  - Large reduction in CPU and memory costs.
  - No need for periodicity.
  - Vacuum is almost free.
  - Chemical information (charge population, projected density of states, etc).

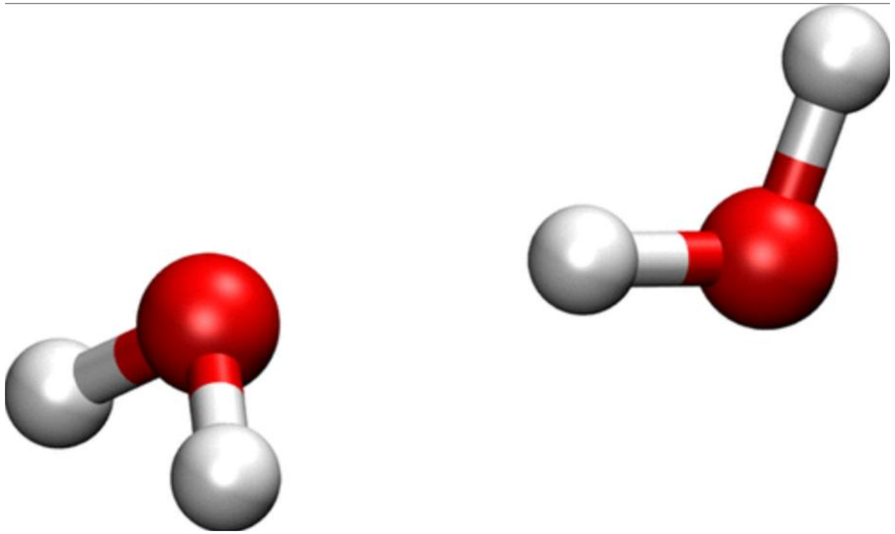
Problems… Localization is a double-edged sword

- Advantages:
  - Very efficient in terms of number of orbitals per electrons.
  - Very well suited to describe localization.
  - Large reduction in CPU and memory costs.
  - No need for periodicity.
  - Vacuum is almost free.
  - Chemical information (charge population, projected density of states, etc).

- Disadvantages:
  - Lack of systematics for convergence.
  - Require human and computational effort to get a good basis set before use.
  - Spatially biased, since they are optimal for an atomic problem: Basis Set Superposition Error.
  - Orbitals move with atoms, which brings extra terms in forces (Pulay corrections).
  - Calculation of Hamiltonian matrix elements can be quite complicated (and expensive).

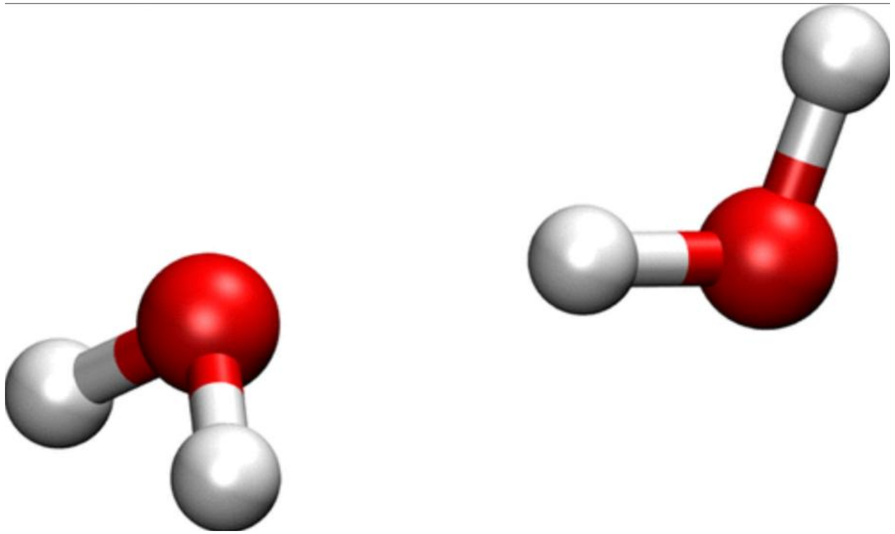
Problems… BSSE

Imagine that you have the following system… and you want to calculate it’s binding energy



Problems… BSSE

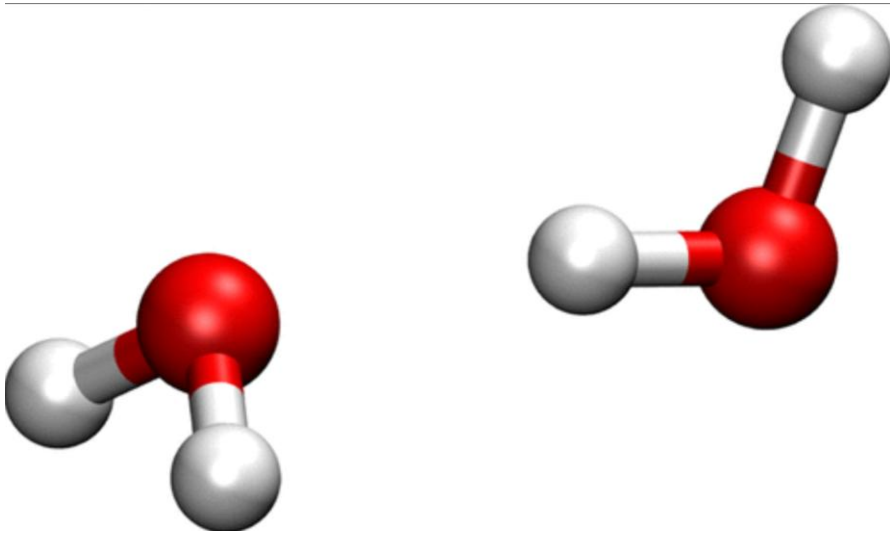
Imagine that you have the following system… and you want to calculate it's binding energy



$$E_{binding} = E_{total} - E_{system_1} - E_{system_2}$$

Problems… BSSE

Imagine that you have the following system… and you want to calculate it's binding energy



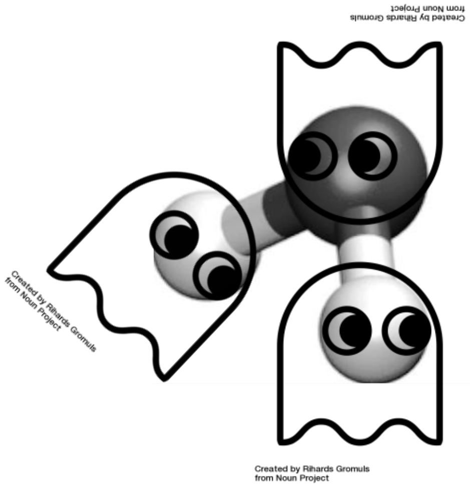
- More flexible basis set as compared to the individual systems.
  (the basis functions coming from neighbouring atoms also help improve the description of the electronic density around one of the atoms)
- Typically it overestimates the interaction energy
  [giving rise to inaccuracies in the binding energy (too large, too stabilizing), adsorption energies and vacancy formation energies]

$$E_{binding} = E_{total} - E_{system_1} - E_{system_2}$$

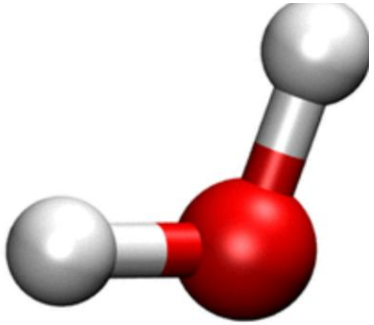
Problems… BSSE… Solution

Problems… BSSE… Solution

Ghost atoms!



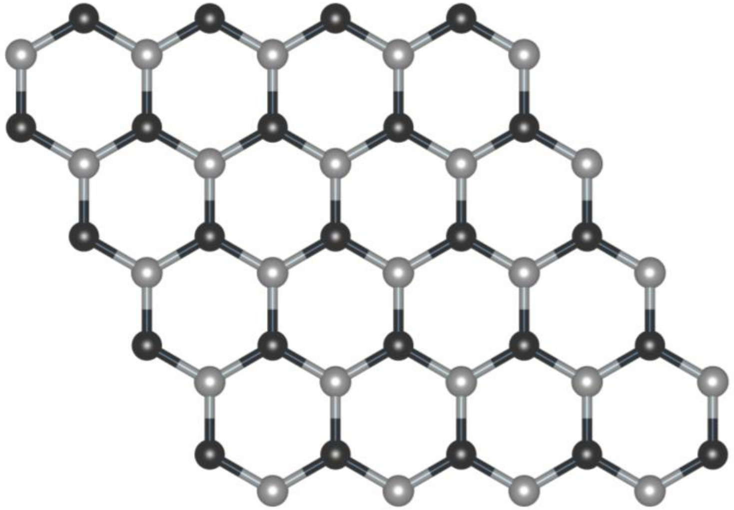
Created by Rihards Gromuls
from Noun Project



- Place basis functions where there are no atoms (more flexibility)
- They do not add charge to the system
- In SIESTA they enter the FDF file in the ChemicalSpeciesLabel block as negative numbers
- If we have better basis sets the improvement by adding ghost atoms lowers.

Problems… 2D materials

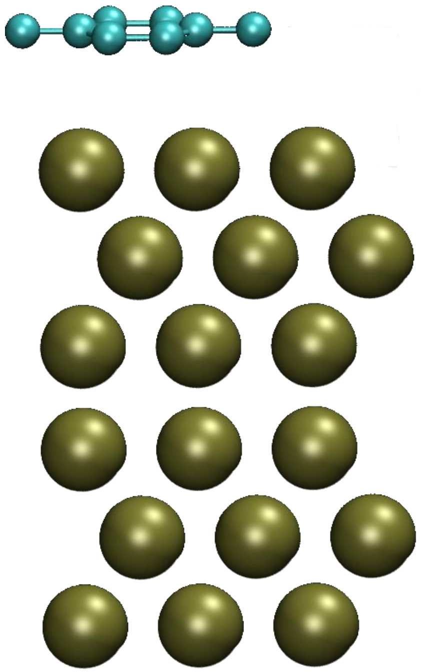
Graphene:



Top view

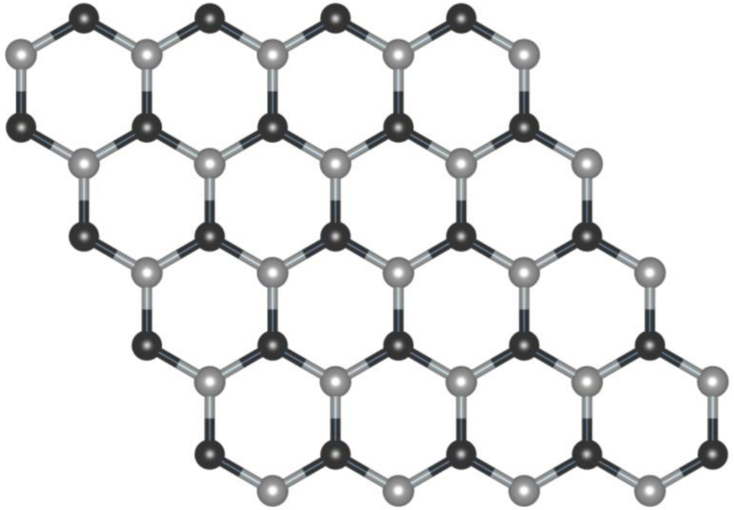
Side view

Graphene
on a substrate

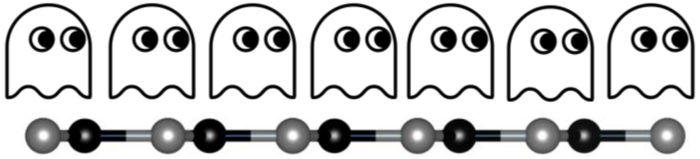


Problems… 2D materials…Solutions

Graphene:

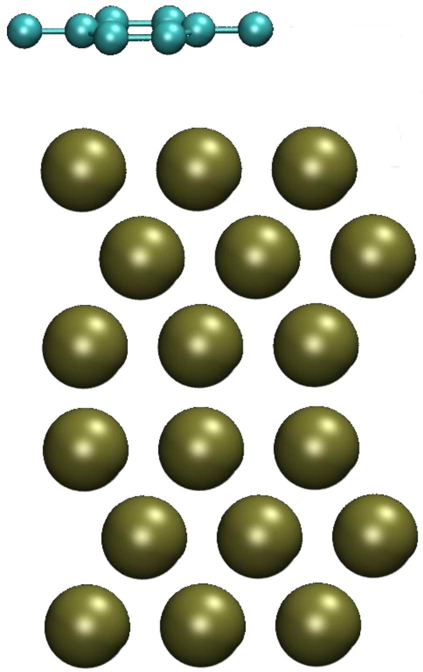


Top view



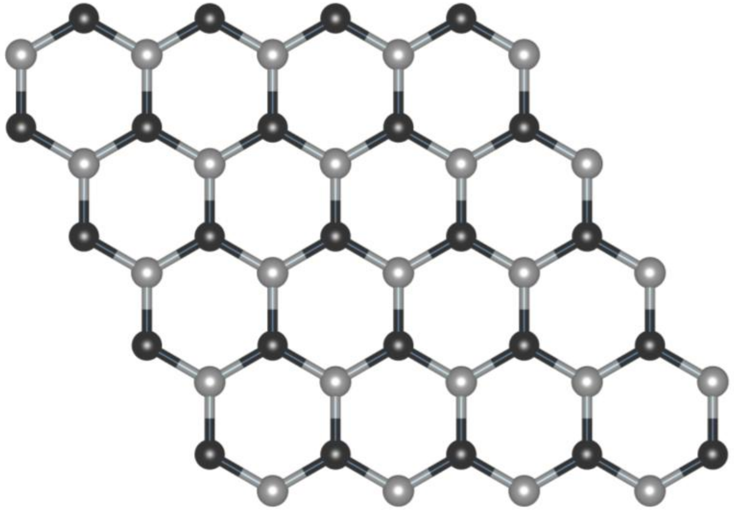
Side view

Graphene
on a substrate



Problems… 2D materials…Solutions 2

Graphene:

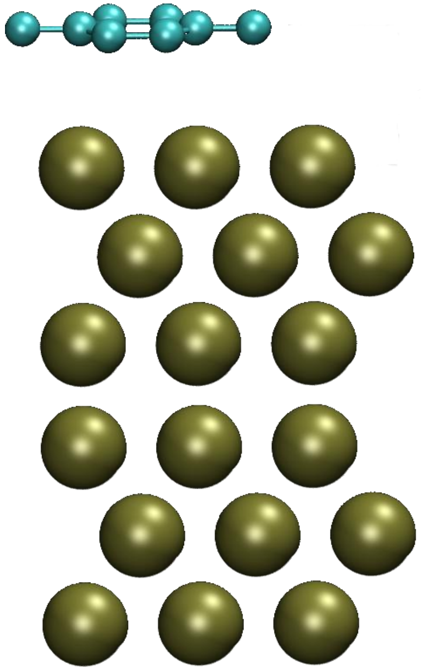


Top view

Add diffuse orbitals

Side view

Graphene
on a substrate



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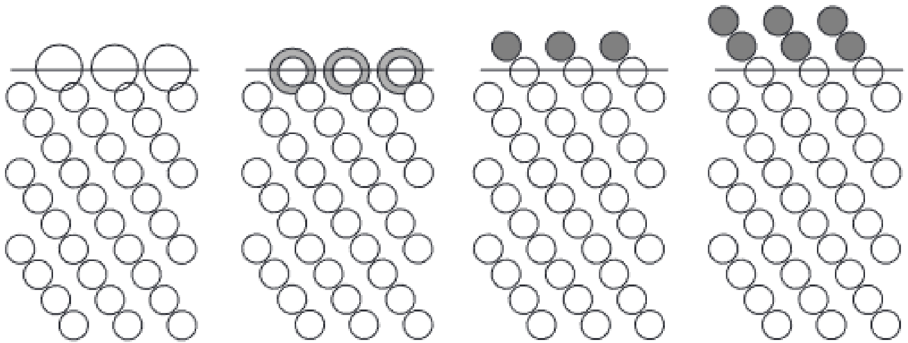
Problems… 2D materials…Diffuse orbitals



(a) Opt. DZP (b) Diffuse (c) 1–Floating (d) 2–Floating

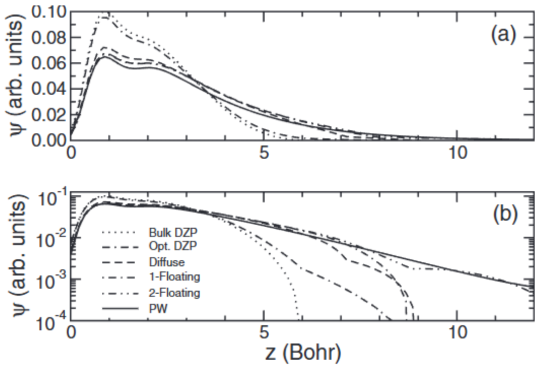


FIG. 7. Decay into the vacuum of the wave function of the surface state at the Γ point for Ag, plotted along a line in the z direction (perpendicular to the surface) which passes through a surface atom. The last atomic layer is located at $z=0$. (a) and (b) show the wave function in linear and logarithmic scale, respectively.

- Very important for surfaces/2D materials
- longer cut-off radii and slower decay than the usual orbitals in bulk materials
- Typically: $l \rightarrow l+1$
  Graphene: 2*s* 2*p* valence → 3*s* 3*p* diffuse orbitals
- Improve the surface energies and work functions
- Improves the energy of the surface states and their decay into vacuum
- They are a bit more expensive than ghost orbitals
- They are more convenient for relaxations (or dynamical calculations) (moving the centers of the ghost orbitals could lead to instabilities in the calculation)

Phys. Rev. B (b) **79**, 075441 (2009)

Hands-on session:
Basis sets…Special cases

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