

Advanced School on  
**QUANTUM MODELLING**  
of Materials with CRYSTAL



UNIVERSITÀ  
DI TORINO

# Local Gaussian-Type Basis Functions for Solids

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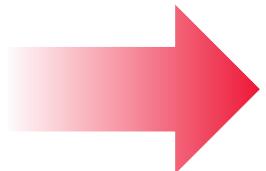
# Outline

- Representation of one-electron **wavefunction in solid-state**:
  - Direct space grids
  - Expansion in **Basis Set**
    - **Plane Waves (PW)**
    - **Local Functions**
- The form of Local functions:
  - **Slater** type
  - **Gaussian** type
    - Contraction
    - Classification and Databases
- **CRYSTAL Input** of Basis set
- **Errors** related to Basis Sets
- **Effective Core Potentials (ECP)**

# One Electron Equations

Electronic  
**Schrödinger Equation**

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)$$



**Cannot be solved**  
for more than 1 e<sup>-</sup>

## Approximations

**Hartree-Fock**

$$\hat{F}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

**KS-DFT**

$$\left[ -\frac{1}{2}\nabla^2 + V_{\text{eff}}[n, \nabla n, \tau, \nabla^2 n, \dots](\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

In both, we need to describe  
the **single-particle orbital**

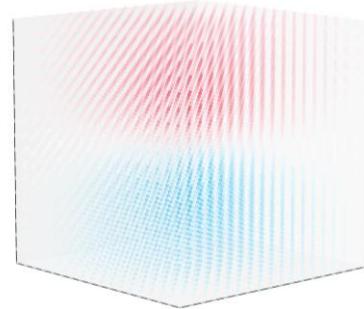
$$\psi_i(\mathbf{r})$$

And obtain the full set  $\{\psi_i(\mathbf{r})\}$

# How to Represent $\psi_i(\mathbf{r})$

## 1. Direct Representation on a Grid (numerical)

Can be accurate, but huge grids required: expensive



## 2. Expansion in Basis Set (algebraic)

Compact, high accuracy, efficient

### Linear Combination of Basis Functions

$$\hat{H}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \quad \xrightarrow{\text{Matrix Equation}} \quad \mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}$$

$$\begin{aligned} \text{Hamiltonian Matrix } \mathbf{H} &\xrightarrow{\text{ }} H_{\mu\nu} = \langle \chi_\mu | H_i | \chi_\nu \rangle \\ \text{Overlap Matrix } \mathbf{S} &\xrightarrow{\text{ }} S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle \end{aligned}$$

$$\psi_i(\mathbf{r}) = \sum_{\mu} c_{\mu i} \chi_{\mu}(\mathbf{r})$$

↗ Size of Basis Set  
 $N_{\text{BS}}$   
↗ Basis Function (known)  
↘ Coefficients (unknown)

# Expansion in a Basis Set

$$\psi_i(\mathbf{r}) = \sum_{\mu}^{N_{\text{BS}}} c_{\mu i} \chi_{\mu}(\mathbf{r})$$

Linear Combination (LC) of  
known Basis Functions

**Basis Set**  $\{\chi_i\}$

What properties should the basis function have?

1. **Analytical form** for easy and accurate **integral** calculation
2. **Rapid convergence** for accurate description of solid electronic bands and charge distributions
3. Allow orderly and **systematic extension** towards completeness with respect to one-electron functions
4. **Orthogonal**, or at least the non-orthogonality should not be a problem

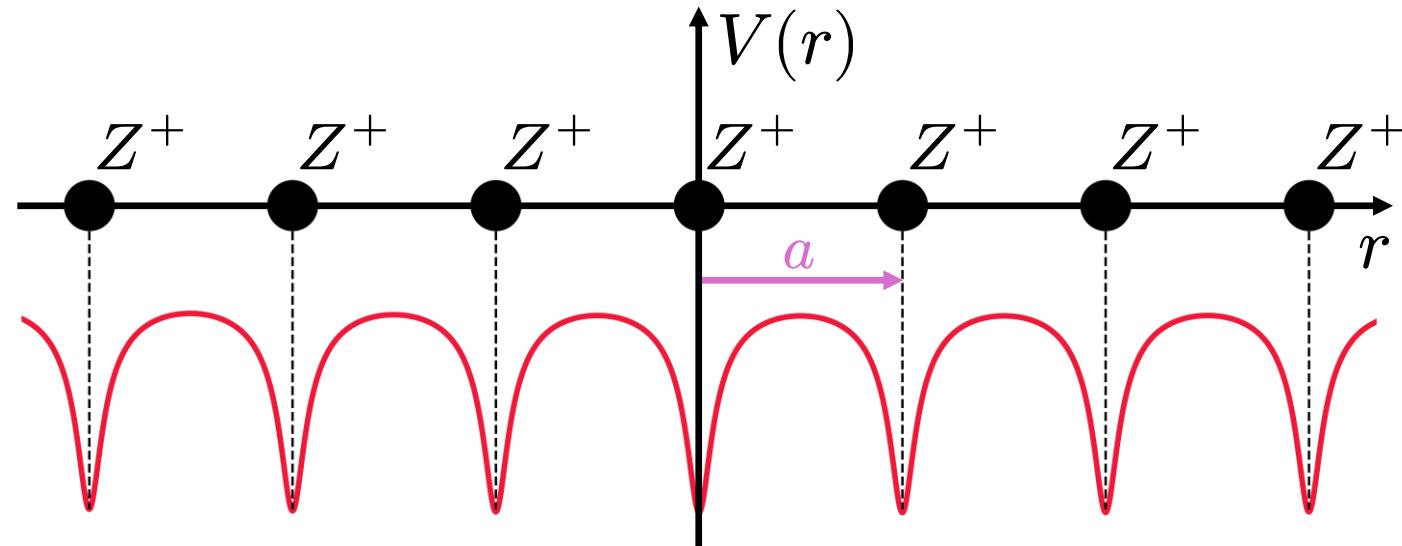
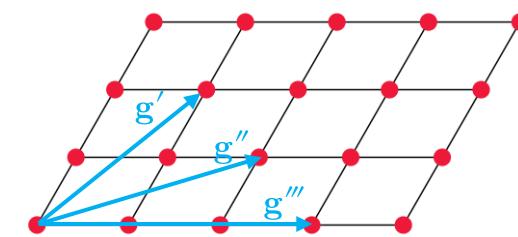
# Periodic Systems

Infinite Periodic Systems → Translational Symmetry in Potential

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{g})$$

**Bravais Lattice Vectors**

Point to any cell in the lattice



The only solution is:

**Bloch's Theorem**

$$\psi_i^k(\mathbf{r}) = u_k(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}$$

Periodic  
(describes only unit cell)

$$u_k(\mathbf{r}) = u_k(\mathbf{r} + \mathbf{g})$$

Phase Factor

**Plane Waves**

**Localized Functions**

# Plane Waves

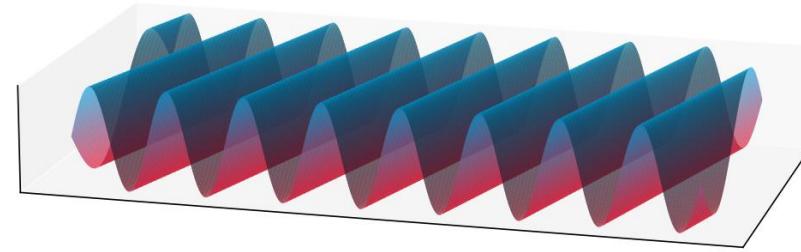
**Bloch's Theorem**  $\psi_i^k(\mathbf{r}) = u_k(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}$

$u_k(\mathbf{r})$  is periodic, so can be written as a linear combination of simple waves (**Fourier Expansion**)

And combining with Bloch's Theorem we get:

$$\psi_i^k(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}} \sum_{\kappa} c_{ik}(\kappa) e^{i\kappa\cdot\mathbf{r}} = \boxed{\sum_{\kappa} c_{ik}(\kappa) e^{-i(\kappa+\mathbf{k})\cdot\mathbf{r}}}$$

$$u_k(\mathbf{r}) = \sum_{\kappa} c_{ik}(\kappa) e^{i\kappa\cdot\mathbf{r}}$$



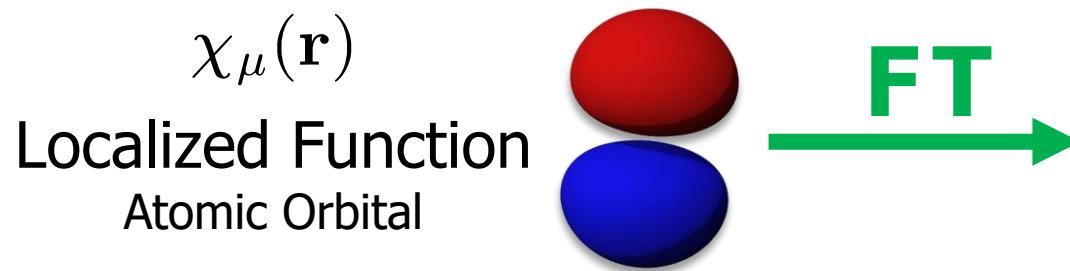
1. Inherently **Bloch Functions**
2. **Orthogonal**
3. Number of PW (basis set quality)  
controlled by a single **energy cutoff**  
→ systematic improvement
4. **Difficult** describe the **electronic structure** near nuclei  
→ **Pseudopotentials** must be used

$$\psi_i^k(\mathbf{r}) = \sum_{\kappa} c_{ik}(\kappa) e^{-i(\kappa+\mathbf{k})\cdot\mathbf{r}}$$

$\frac{1}{2}|\mathbf{k}+\kappa|^2 \leq E_{\text{cut}}$

Examples:  
**Quantum ESPRESSO,**  
**VASP,** **CASTEP**

# Localized Functions



Bloch Function  
Periodic

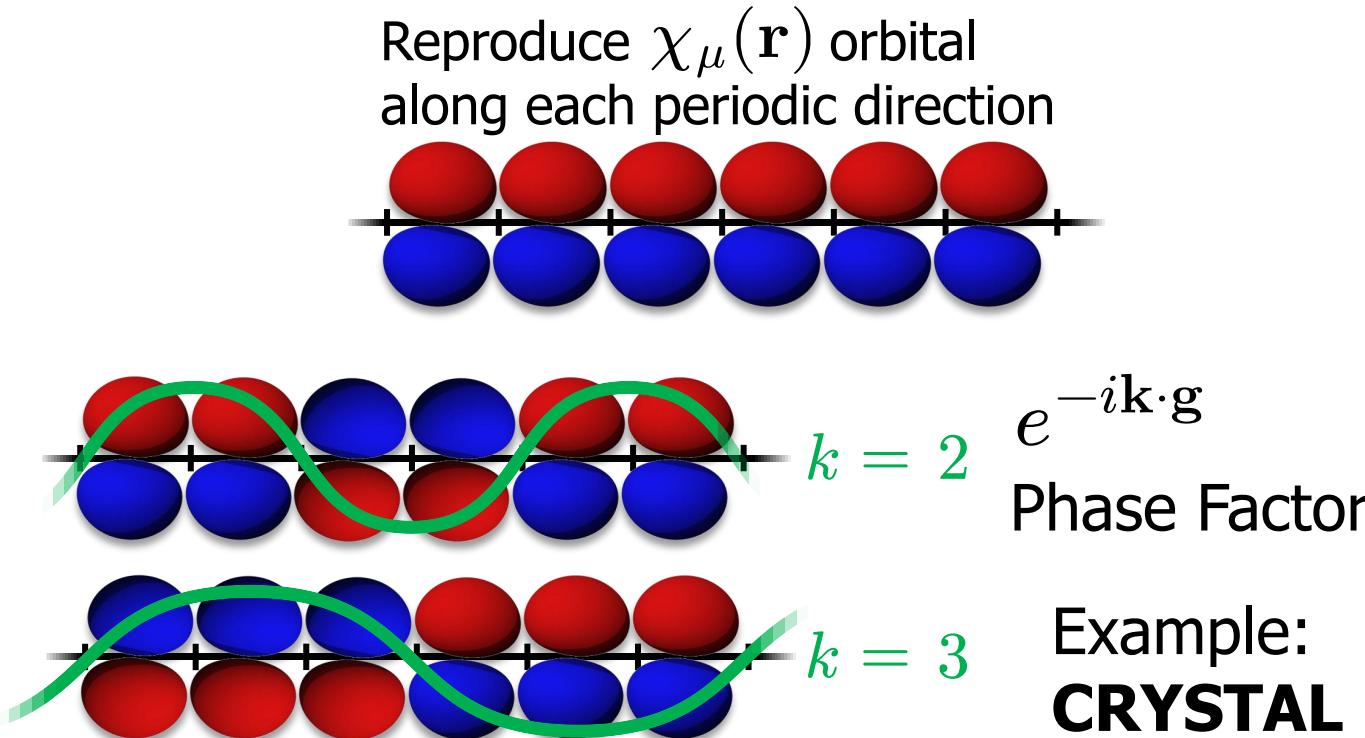
$$\phi_\mu^k(\mathbf{r}) = \sum_{\mathbf{g}} \chi_\mu(\mathbf{r} - \mathbf{t}_\mu - \mathbf{g}) e^{-i\mathbf{k}\cdot\mathbf{g}}$$

Lattice Vectors  
Atomic Position

**Crystalline Orbital** as Linear Combination of **Bloch Functions**

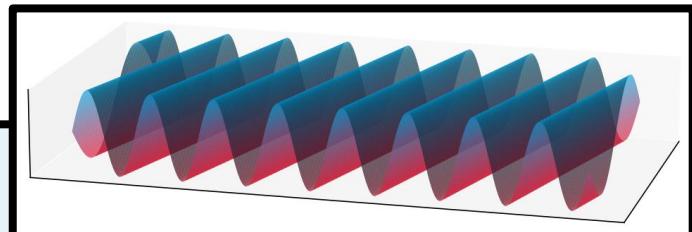
$$\psi_i^k(\mathbf{r}) = \sum_{\mu} c_{\mu i}^k \phi_\mu^k(\mathbf{r})$$

1. Functions localized on **atomic position**
2. Correspond to the **LCAO** approximation
3. **All-electron** or pseudopotential
4. **Easier** implementation of **integrals**
5. **Non-orthogonal**



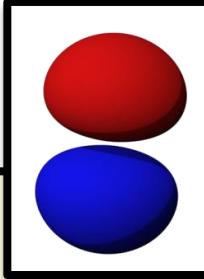
# Plane Waves vs Local BS

PW



- Universal
- Need Pseudopotentials
- Large number of PWs needed
- Non Local
  - **Loss of chemical insight**
- Systematic improvements (with  $E_{\text{cut}}$ )
- Numerical efficient
- 3D periodic replicas for 2D, 1D and molecules
- No basis set Superposition Error
- Expensive hybrid calculations

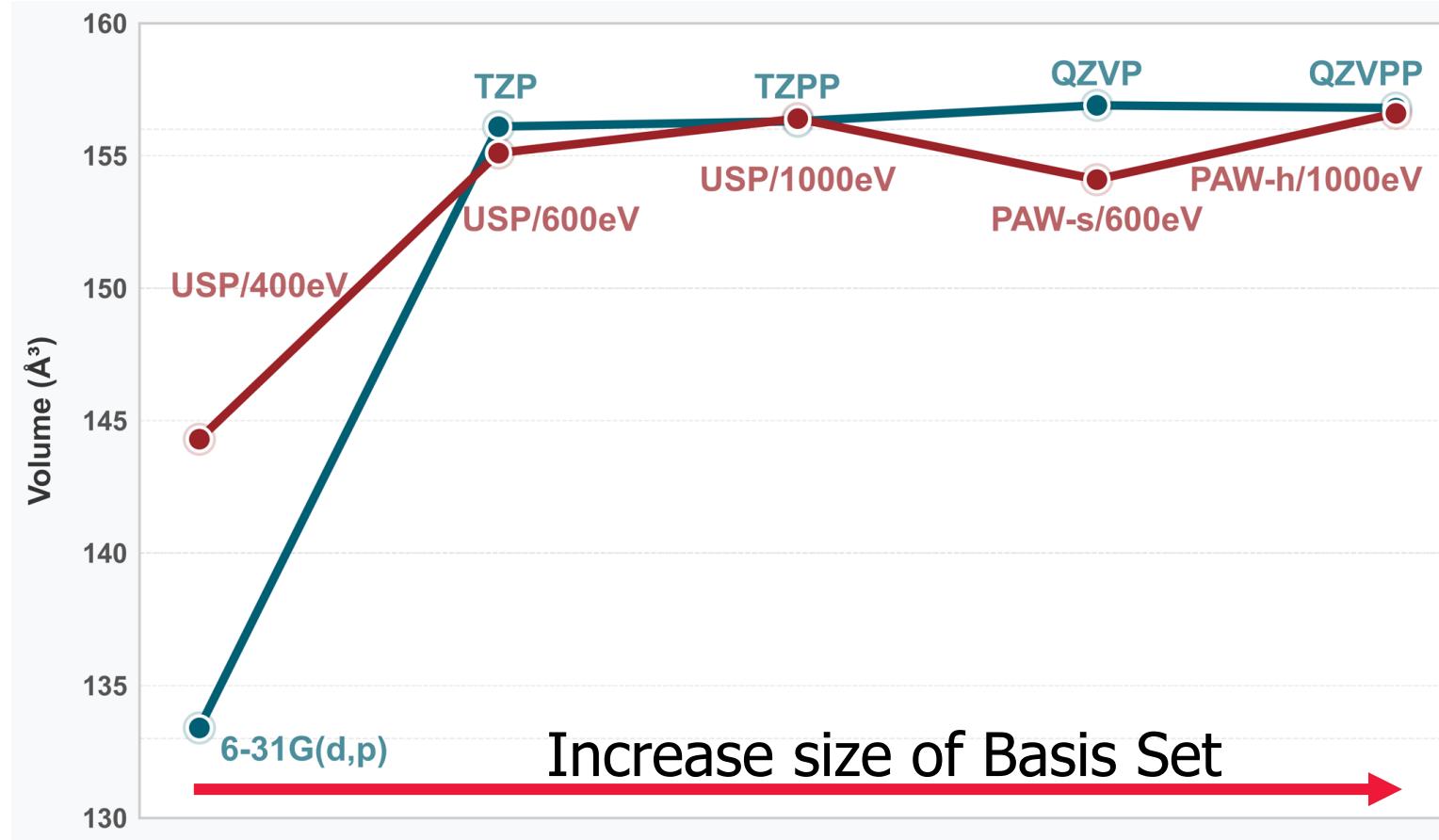
Local BS



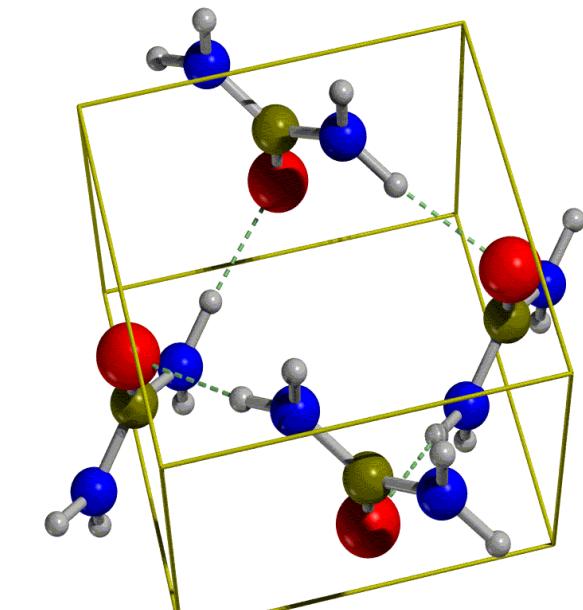
- Element Specific
- All-electron and Pseudopotentials
- Small Basis Set can give accurate results
- Local
  - **Chemical insight is given**
- Systematic improvement not easy
- Computational efficient
- No artificial replica for 2D, 1D and molecules
- Basis Set Errors
- Efficient Hybrid Calculations

# Comparing Results

## Optimized Cell Volume



Local orbitals  
Plane waves



Urea  
Molecular Crystal

# Local Basis Functions: Form

Solution of the Schrödinger equation for hydrogen-like atoms

$$\chi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi)$$

**Radial Function**

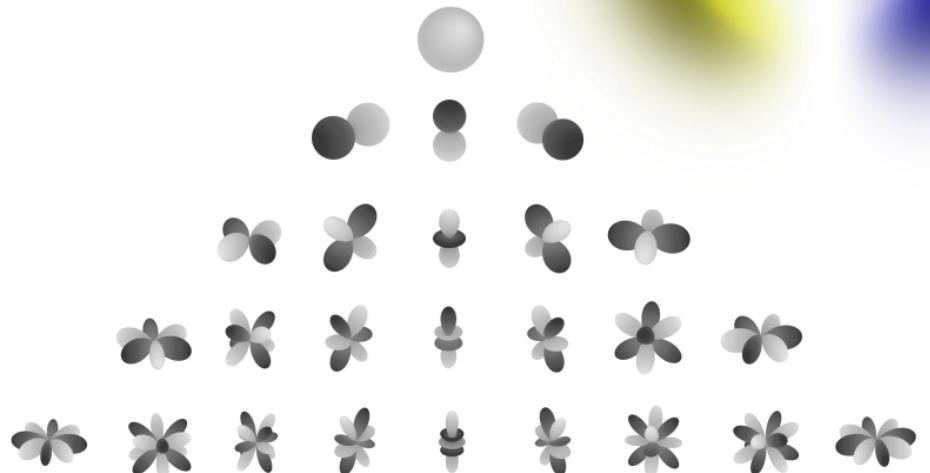
$$R_{nl}(r) = N_{nl}\rho^l L_{n+1}^{2l+1}(\rho)e^{-\rho/2}$$

**Angular Function**

$$Y_{lm}(\theta, \varphi)$$

Real Spherical Harmonics

1. Functions **centered on atoms**
  2. AO are base of **Molecular Orbital theory**
  3. Nice representation of “final” solution (CO)
- **Fewer function required** ( $\sim 10/100$ )  
 $[PW \sim 1\,000/1\,000\,000]$



# Local Basis Functions: Radial Form

## Slater-Type Orbitals (STO)

$$R_{nl}^{\text{STO}}(r) = N_{nl} r^{n-1} e^{-\zeta r}$$

$$\chi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_{lm}(\theta, \varphi)$$

Hydrogen Orbital like behaviour:

1. **Fast** convergence
2. Core region correctly described (**cusp**)
3. Not ideal for integrals

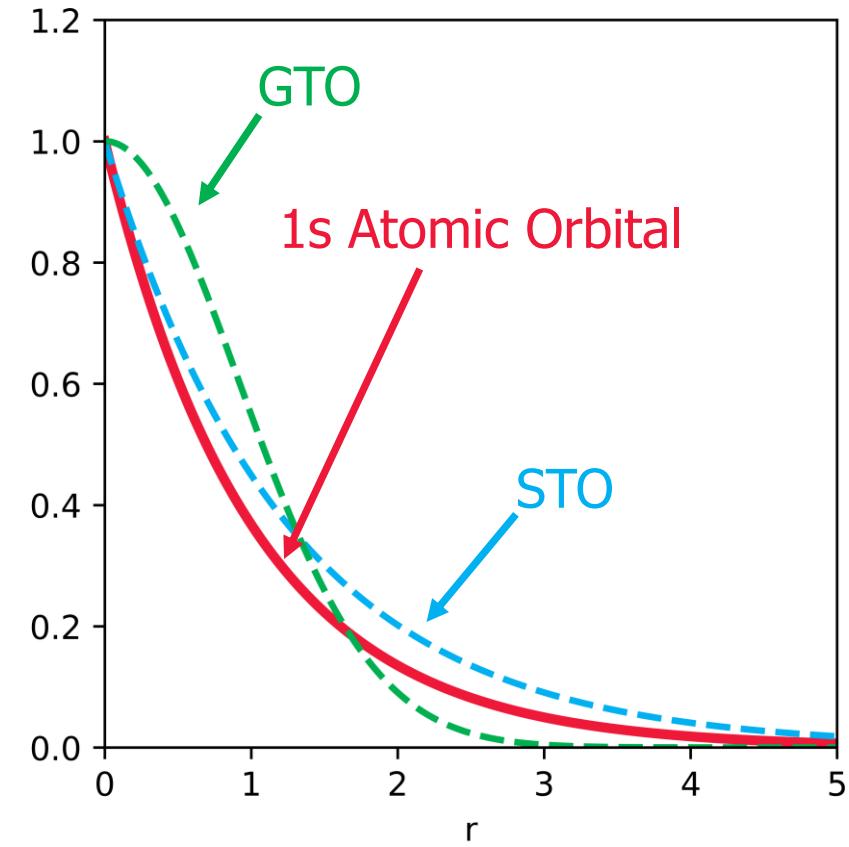
## Gaussian-Type Orbital (GTO)

$$R_{nl}^{\text{GTO}}(r) = N_{nl} r^{2n-l-2} e^{-\alpha r^2}$$

Wrong behaviour:

1. **Slow** convergence
2. No **cusp**, too fast decay
3. Easier for integrals

→ product of two gaussians is still a gaussian



# Gaussian-type Basis Functions

## Spherical Gaussian Functions

$$\chi_{nlm}^{\text{spher}}(r, \theta, \varphi) = N_{nlm} Y_{lm}(\theta, \varphi) r^{2n-l-2} e^{-\alpha r^2}$$

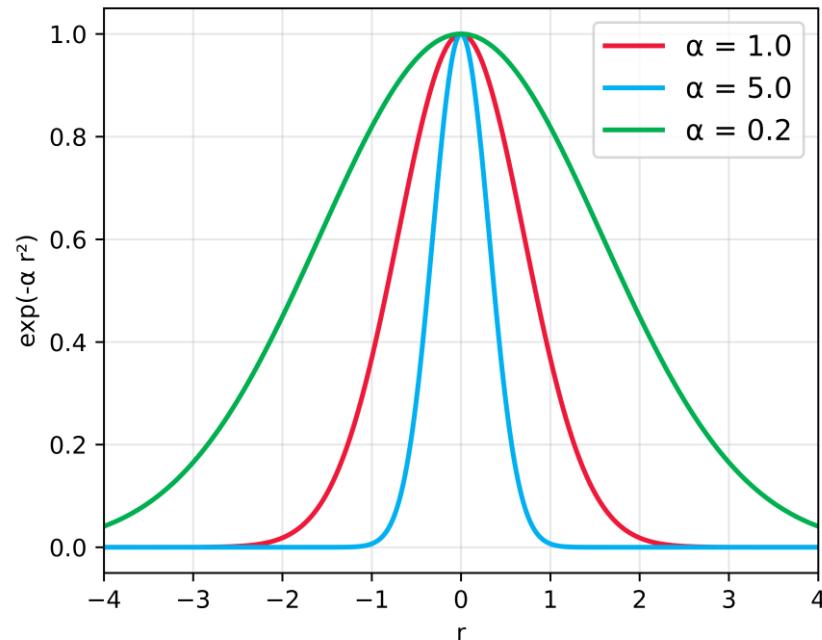
1. No spurious elements  
→ **smaller** basis set
2. Less problems of linear dependency
3. **Exact** rotational **symmetry**

## Cartesian Gaussian Functions

$$\chi_{nlm}^{\text{cart}}(x, y, z) = N_{nlm} x^{l_x} y^{l_y} z^{l_z} e^{-\alpha r^2}$$

1. Contain **spurious component**  
→ more BFs than needed (more expensive)
2. **Nonphysical**
3. Reduced rotational symmetry
4. **Easier** to deal with ( $x, y, z$  can be separated)

$\alpha$  is **exponent** parameter  
Large: tight function    Small: diffuse function

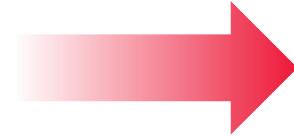


$$l = l_x + l_y + l_z$$

$l_x, l_y, l_z$  are integers that add up to quantum number  $l$

# Primitive and Contracted GTO

Recover the **cusp** problem  
 Better describe **tails**



**Fixed Linear Combination** (contraction)  
 of **Primitive** Gaussian functions (G)

## Contracted GTO

$$\chi_{\mu}(\mathbf{r}) = \sum_j^{N_G} d_{\mu j} G(\mathbf{r}; \alpha_{\mu j})$$

$$G(\mathbf{r}; \alpha_{\mu}) = N Y(\theta, \varphi) r^{2n-1-2} e^{-\alpha_{\mu j} r^2}$$

Primitives share the same:

1. Center (nuclear position)
2. Angular momentum

$\alpha_{\mu j}$  Contraction **Exponents**

$d_{\mu j}$  Contraction **Coefficients**

**TOTAL BASIS SET** →

Finite **list** of all **exponents** and  
**coefficients** for each **atomic species**

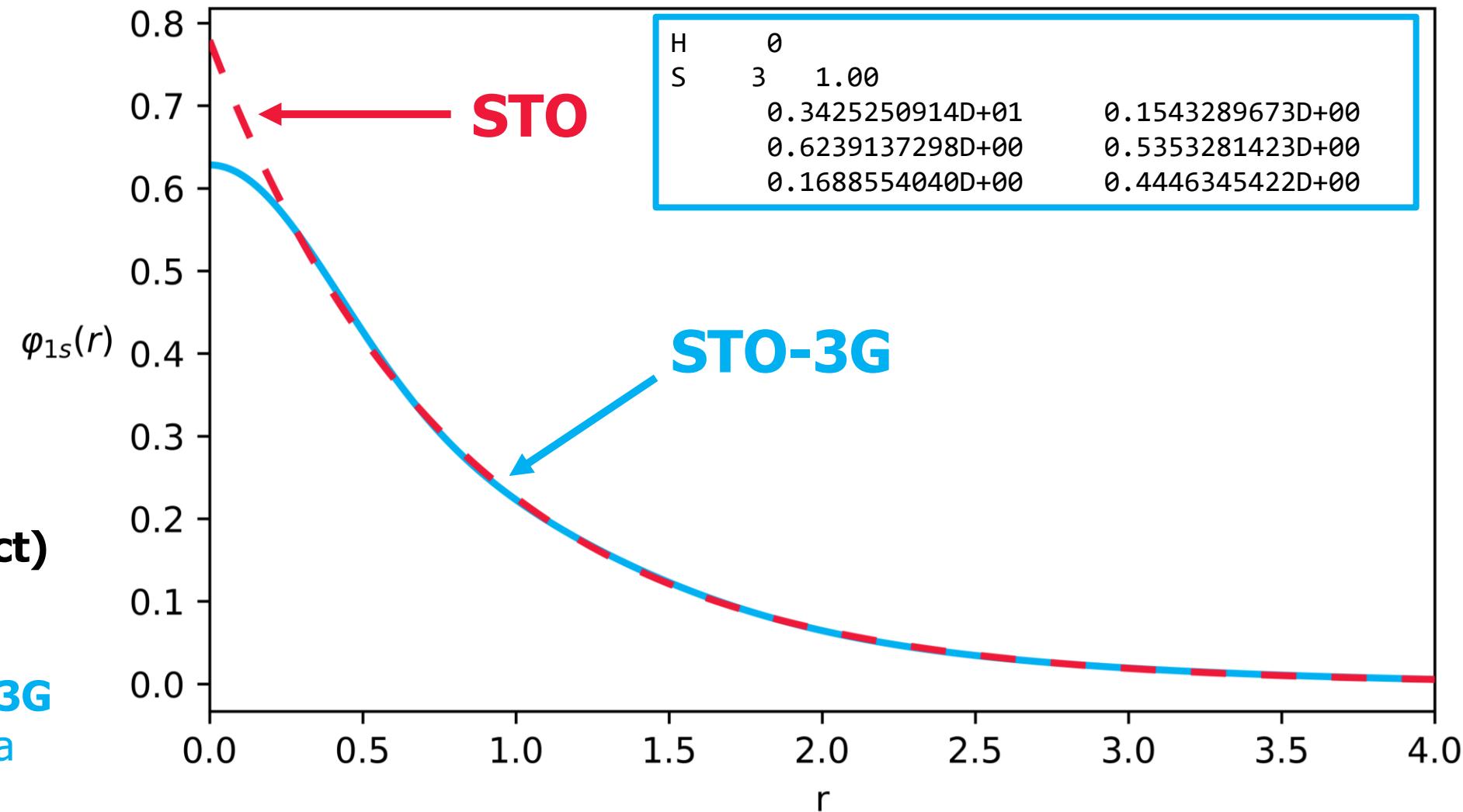
# Example of Contraction

H atom, 1s Orbital

$$N_G = 3$$

Energy (exact)  
-0.5 Ha

Energy STO-3G  
-0.49491 Ha



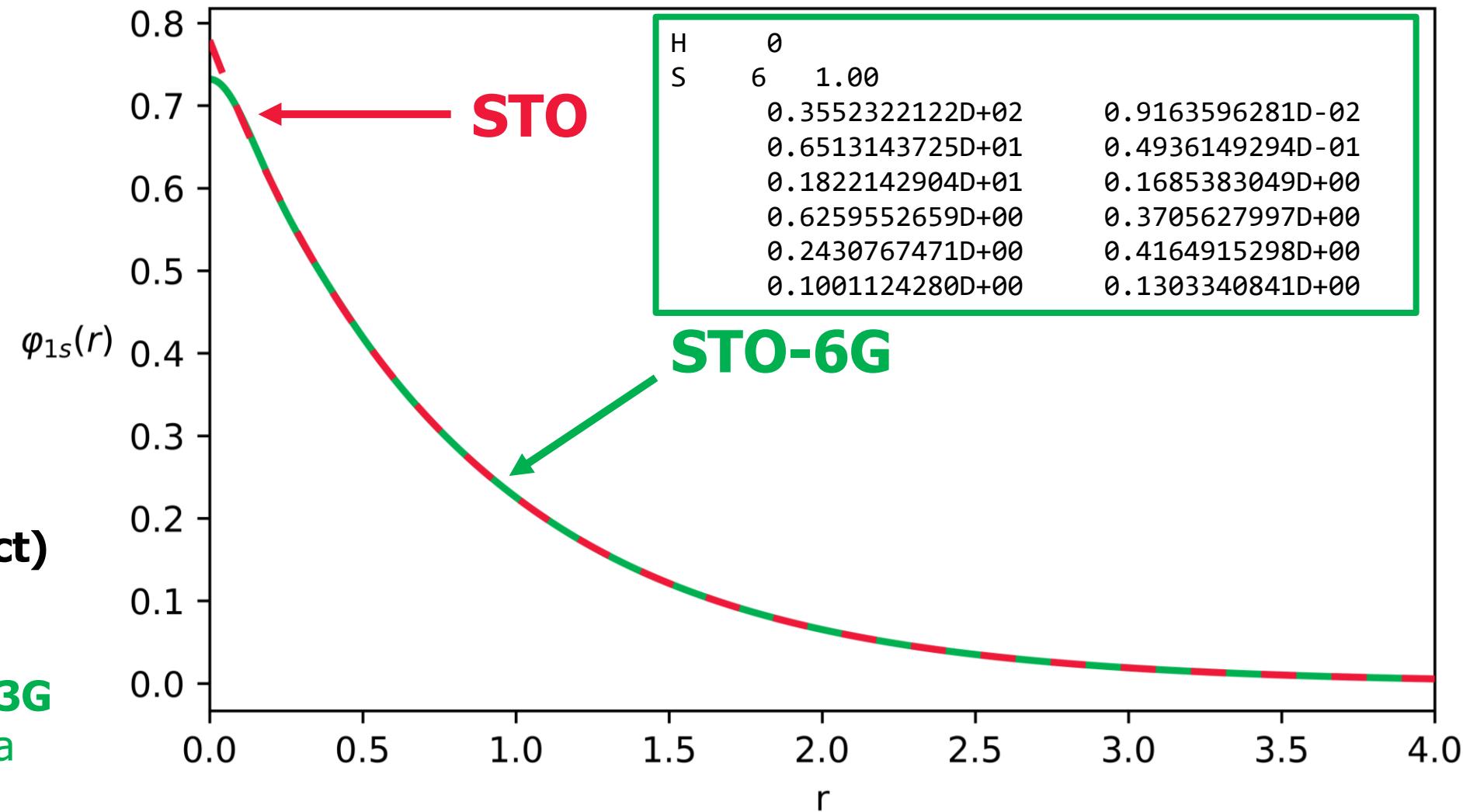
# Example of Contraction

H atom, 1s Orbital

$$N_G = 6$$

Energy (exact)  
-0.5 Ha

Energy STO-3G  
-0.49983 Ha



# Classification of GTO Basis Sets

## Minimal basis set (or single-zeta, **SZ**)

Single basis function for each occupied orbital

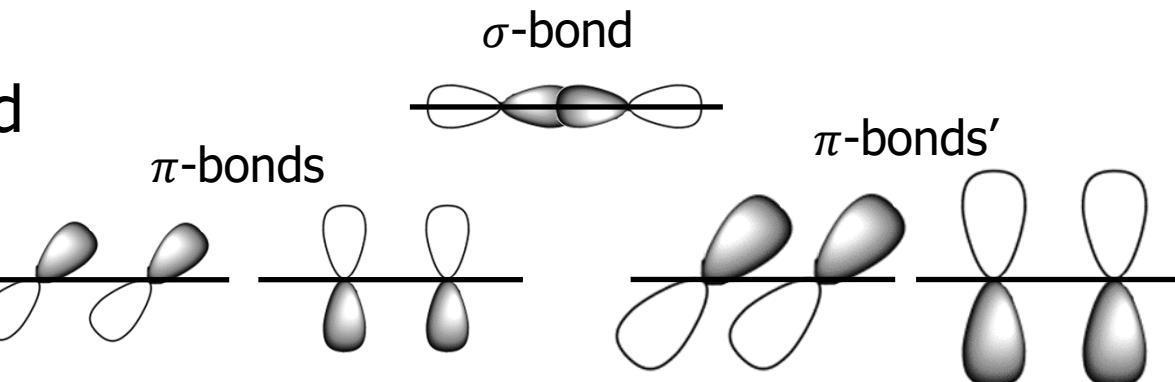
## Double-Zeta (**DZ**)

Two basis function for each occupied orbital

- **extend** the basis
- crucial **physical** and **chemical relevance**

### Example: C-C Triple Bond

- Tighter  $2p_z$  function is enough for the  $\sigma$ -bond
- More diffuse  $2p_x$  and  $2p_y$  functions are better for electron distribution of  $\pi$ -bonds



 *Doubling all basis functions gives more “flexibility” than the minimal BS*

# Classification of GTO Basis Sets

## Triple-Zeta (TZ)

Three basis function for each occupied orbital

H: 1s, 1s', 1s"

C: 1s, 1s', 1s'', 2s, 2s', 2s'', 2p<sub>x,y,z</sub>, 2p<sub>x,y,z'</sub>, 2p<sub>x,y,z''</sub>

## Quadruple-Zeta (QZ), Quintuple-Zeta (5Z), etc.

→ How many functions do we need?

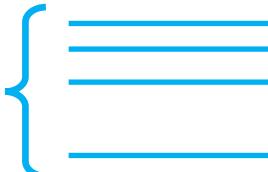
**Bonding** occurs between **valence** electrons

## Split-Valence (V, SV)

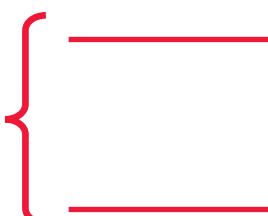
Minimal basis for core orbitals, double/triple/... basis for valence orbitals

→ **DZV**, **TZV**, etc.

VALENCE



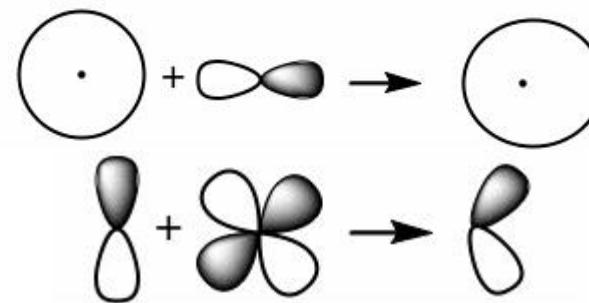
CORE



# Classification of GTO Basis Sets

## Polarization Functions (P)

Angular momentum not occupied in the atom



### Example:

- H, He:           occ. **s**-orbitals   → **p**-type functions
- 1<sup>st</sup> - 2<sup>nd</sup> rows:   occ. **p**-orbitals   → **d**-type functions
- TM:              occ. **d**-orbitals   → **f**-type functions
- Lanthanides:     occ. **f**-orbitals   → **g**-type functions

Available since  

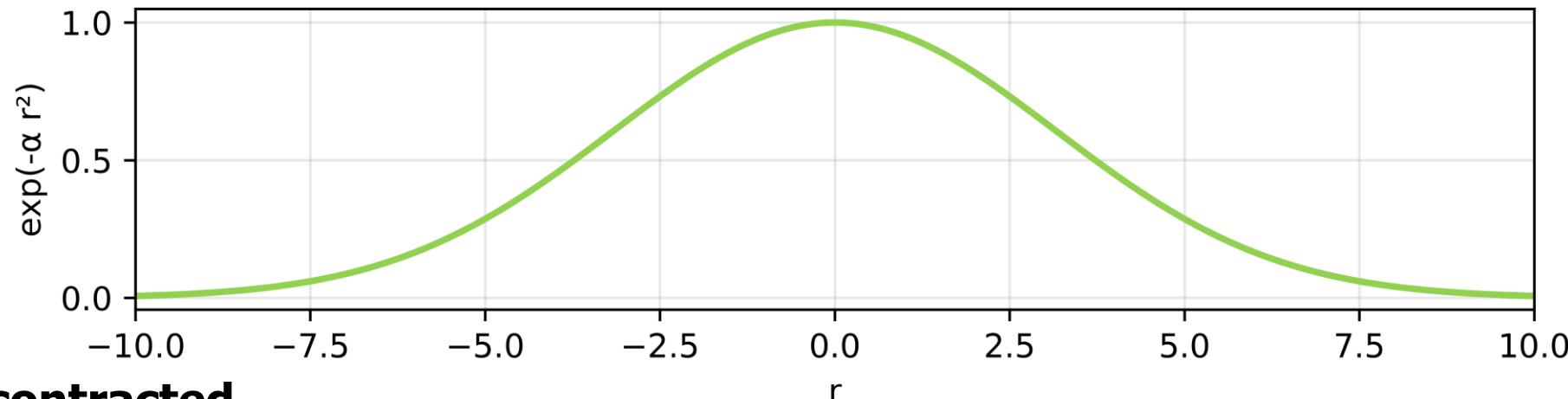

Important to describe polarized electronic charge distributions (ECD) (e.g. **polar bonds**, **dipole moment**, **polarizability**, **dielectric response**, anisotropy of ECD upon **cell deformation**, **H-bonding**, correlation energy)

→ **DZVP**, **TZVP**, etc.

# Classification of GTO Basis Sets

## Diffuse Functions (+, D, aug-)

Small  $\alpha$  exponents ( $< 0.1 \text{ bohr}^{-2}$ )



Usually **uncontracted**

Useful to described the **tail** of the ECD, **anions**, **Rydberg states**, **metals**, **surfaces**, **weak interactions**

**WARNING:**

Diffuse functions in **solids** can cause **numerical instabilities**  
**Avoid** exponents lower than **0.1 ... 0.07 a.u.**

Apart from specific case, they are generally NOT necessary in solids

# Gaussian Basis Set Notation

## Typical notation:

(Primitive set) / [Contracted set]

(s, p, ... primitives) / [s, p, ... contractions]

### Example: (10s4p) / [3s2p]

- 10 s primitives → 3 s contracted func.
- 4 p primitives → 2 p contracted func.

## In addition:

{Contraction scheme}

### Example: {631/31}

- 3 s contracted func. → 6 G 3 G 1G
- 2 p contracted func. → 3 G 1 G

Quality	Label	Name
DZP	Pople	STO-3G
	Pople	3-21G
	Jensen	pc-0
	Pople	6-31G*
	Ahlrichs	Def2-SV(P)
	Ahlrichs	Def2-SVP
	Jorge	DZP
	Sapporo	DZP
	Roos	ANO-DZP
	Dunning	cc-pVDZ <sup>1</sup>
	Petersson	2ZaP
	Jensen	pc-1
TZP	Pople	6-311G(2df)
	Ahlrichs	Def2-TZVP
	Ahlrichs	Def2-TZVPP
	Jorge	TZP
	Sapporo	TZP
	Roos	ANO-TZP
	Dunning	cc-pVTZ
	Petersson	3ZaP
	Jensen	pc-2
	Ahlrichs	Def2-QZVP
	Ahlrichs	Def2-QZVPP
	Sapporo	QZP
QZP	Roos	ANO-QZP
	Dunning	cc-pVQZ
	Jensen	pc-3
	Dunning	cc-pV5Z
	Jensen	pc-4
5ZP		

Examples of common families of *molecular* BSs

Usually, BSs are known *by their names*

# CRYSTAL Input

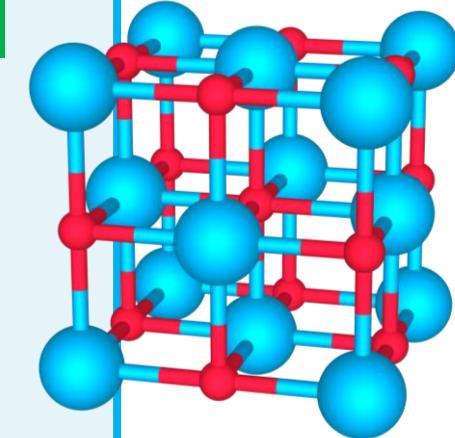
Example: MgO STO-3G

```

12 3
0 0 3 2. 1.
 2.992E+02  1.543E-01
 5.451E+01  5.353E-01
 1.475E+01  4.446E-01
0 1 3 8. 1.
 1.512E+01 -9.997E-02  1.559E-01
 3.514E+00  3.995E-01  6.077E-01
 1.143E+00  7.001E-01  3.920E-01
0 1 3 2. 1.
 1.395E+00 -2.196E-01  1.059E-02
 3.893E-01  2.256E-01  5.952E-01
 1.524E-01  9.004E-01  4.620E-01
8 2
0 0 3 2. 1.
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 2.381E+01  5.353E-01
 6.444E+00  4.446E-01
0 1 3 6. 1.
 5.033E+00 -9.997E-02  1.559E-01
 1.170E+00  3.995E-01  6.077E-01
 3.804E-01  7.001E-01  3.920E-01
99 0
END

```

Atomic Number	Number of Shells



# CRYSTAL Input

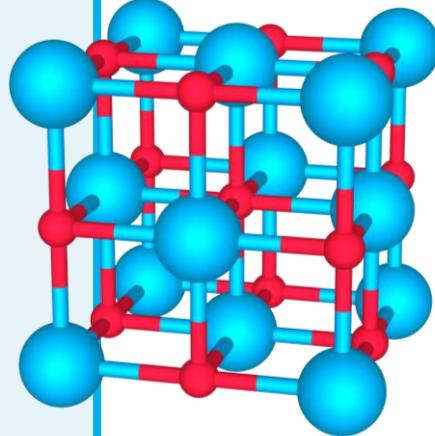
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99 0
END

```

Atomic Number	Number of Shells
	Custom BS Input



# CRYSTAL Input

## Example: MgO STO-3G

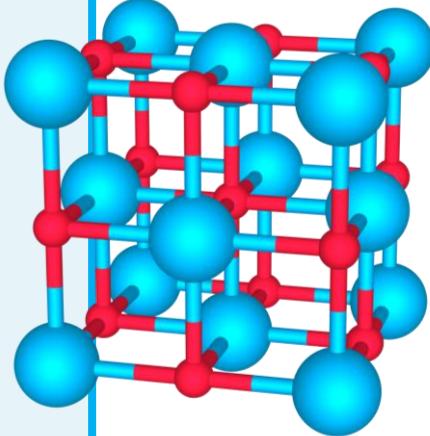
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 3.804E-01  7.001E-01  3.920E-01
99 0
END

```

Atomic Number      Number of Shells  
Custom BS Input  
Shell Type

0	s
1	sp
2	p
3	d
4	f
5	g



# CRYSTAL Input

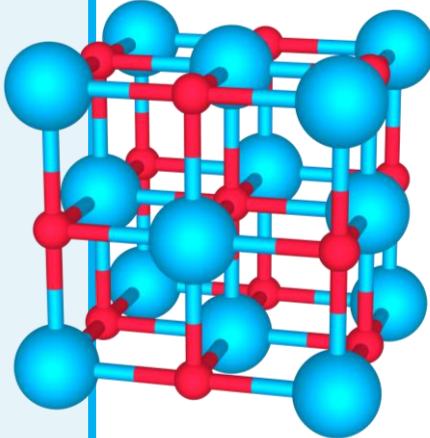
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```

Atomic Number      Number of Shells  
Custom BS Input  
Shell Type  
Number of Primitives



# CRYSTAL Input

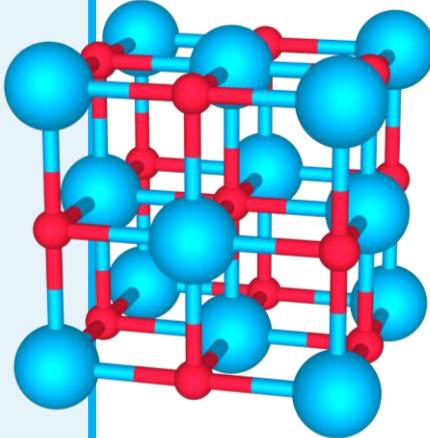
## Example: MgO STO-3G

```

12 3
 0 0 3 2. 1.
  2.992E+02  1.543E-01
  5.451E+01  5.353E-01
  1.475E+01  4.446E-01
 0 1 3 8. 1.
  1.512E+01 -9.997E-02  1.559E-01
  3.514E+00  3.995E-01  6.077E-01
  1.143E+00  7.001E-01  3.920E-01
 0 1 3 2. 1.
  1.395E+00 -2.196E-01  1.059E-02
  3.893E-01  2.256E-01  5.952E-01
  1.524E-01  9.004E-01  4.620E-01
8 2
 0 0 3 2. 1.
  1.307E+02  1.543E-01
  2.381E+01  5.353E-01
  6.444E+00  4.446E-01
 0 1 3 6. 1.
  5.033E+00 -9.997E-02  1.559E-01
  1.170E+00  3.995E-01  6.077E-01
  3.804E-01  7.001E-01  3.920E-01
99 0
END

```

**Atomic Number      Number of Shells**  
**Custom BS Input**  
**Shell Type**  
**Number of Primitives**  
**Occupation (number of electrons)**



# CRYSTAL Input

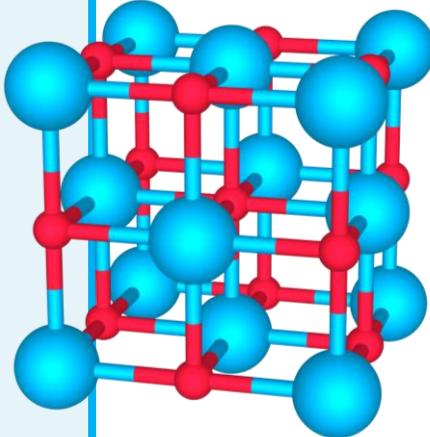
## Example: MgO STO-3G

```

12 3
 0 0 3 2. 1.
    2.992E+02  1.543E-01
    5.451E+01  5.353E-01
    1.475E+01  4.446E-01
 0 1 3 8. 1.
    1.512E+01 -9.997E-02  1.559E-01
    3.514E+00  3.995E-01  6.077E-01
    1.143E+00  7.001E-01  3.920E-01
 0 1 3 2. 1.
    1.395E+00 -2.196E-01  1.059E-02
    3.893E-01  2.256E-01  5.952E-01
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    2.381E+01  5.353E-01
    6.444E+00  4.446E-01
 0 1 3 6. 1.
    5.033E+00 -9.997E-02  1.559E-01
    1.170E+00  3.995E-01  6.077E-01
    3.804E-01  7.001E-01  3.920E-01
99 0
END

```

**Atomic Number      Number of Shells**  
**Custom BS Input**  
**Shell Type**  
**Number of Primitives**  
**Occupation (number of electrons)**  
**Scaling Factor**



# CRYSTAL Input

## Example: MgO STO-3G

```

12 3
 0 0 3 2. 1.
    2.992E+02  1.543E-01
    5.451E+01  5.353E-01
    1.475E+01  4.446E-01

 0 1 3 8. 1.
    1.512E+01 -9.997E-02  1.559E-01
    3.514E+00  3.995E-01  6.077E-01
    1.143E+00  7.001E-01  3.920E-01

 0 1 3 2. 1.
    1.395E+00 -2.196E-01  1.059E-02
    3.893E-01  2.256E-01  5.952E-01
    1.524E-01  9.004E-01  4.620E-01

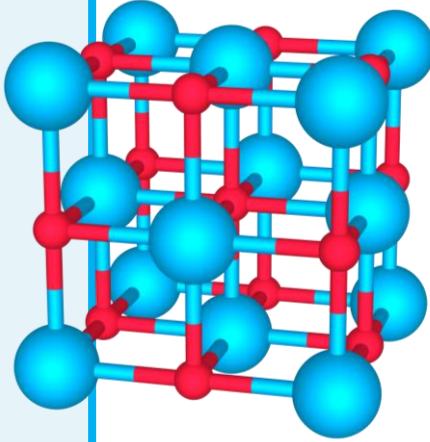
 8 2
 0 0 3 2. 1.
    1.307E+02  1.543E-01
    2.381E+01  5.353E-01
    6.444E+00  4.446E-01

 0 1 3 6. 1.
    5.033E+00 -9.997E-02  1.559E-01
    1.170E+00  3.995E-01  6.077E-01
    3.804E-01  7.001E-01  3.920E-01

99 0
END

```

Atomic Number      Number of Shells  
Custom BS Input  
Shell Type  
Number of Primitives  
Occupation (number of electrons)  
Scaling Factor  
Exponents      Coefficients



# CRYSTAL Input

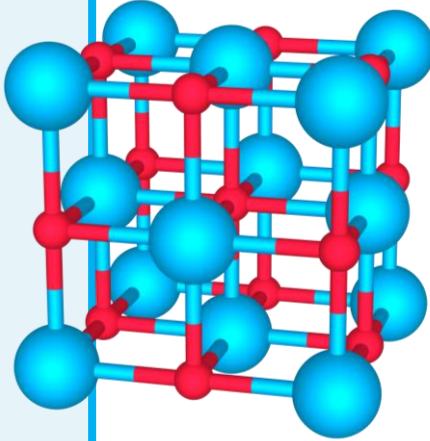
## Example: MgO STO-3G

```

12 3
 0 0 3 2. 1.
    2.992E+02  1.543E-01
    5.451E+01  5.353E-01
    1.475E+01  4.446E-01
 0 1 3 8. 1.      s      p
    1.512E+01 -9.997E-02  1.559E-01
    3.514E+00  3.995E-01  6.077E-01
    1.143E+00  7.001E-01  3.920E-01
 0 1 3 2. 1.
    1.395E+00 -2.196E-01  1.059E-02
    3.893E-01  2.256E-01  5.952E-01
    1.524E-01  9.004E-01  4.620E-01
8 2
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    2.381E+01  5.353E-01
    6.444E+00  4.446E-01
 0 1 3 6. 1.
    5.033E+00 -9.997E-02  1.559E-01
    1.170E+00  3.995E-01  6.077E-01
    3.804E-01  7.001E-01  3.920E-01
99 0
END

```

Atomic Number      Number of Shells  
Custom BS Input  
Shell Type  
Number of Primitives  
Occupation (number of electrons)  
Scaling Factor  
Exponents      Coefficients



# CRYSTAL Input

## Example: MgO STO-3G

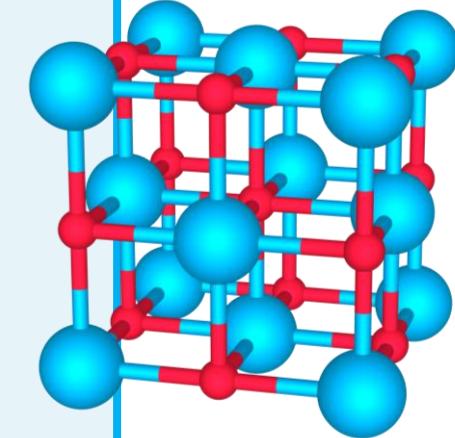
```

12 3
 0 0 3 2. 1.
  2.992E+02  1.543E-01
  5.451E+01  5.353E-01
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 0 1 3 8. 1.
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  1.170E+00  3.995E-01  6.077E-01
  3.804E-01  7.001E-01  3.920E-01
99 0
END

```

Atomic Number      Number of Shells  
Custom BS Input  
Shell Type  
Number of Primitives  
Occupation (number of electrons)  
Scaling Factor  
Exponents      Coefficients

**Close Basis Set**



# Errors Related to Basis Sets

## Basis Set Balancing Error (BSBE)

Basis sets must be of **same quality** both in the same system and when comparing energies of two systems (trivial)

## Basis Set Incompleteness Error (BSIE)

Near-complete basis set is unaffordable → too many basis functions

Complete Basis Set (CBS) limit → **hierarchical BS** and **extrapolation**

Possible for molecule, more **delicate for solids**

## Basis Set Superposition Error (BSSE)

Artificial **overestimation** of binding energies

More relevant for **densely packed solids** and **small basis sets**

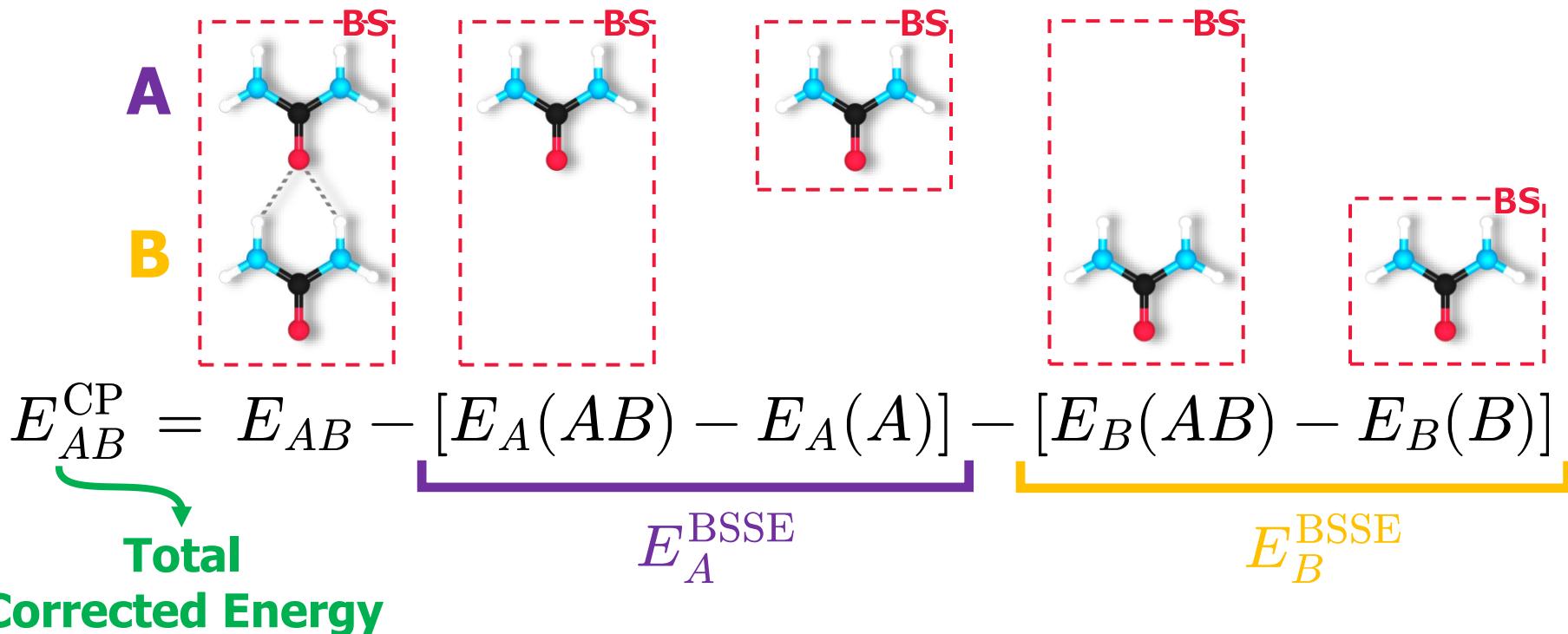
Corrections are needed

# Basis Set Superposition Error

On system **AB**, with a *finite* basis set:

→ Description of fragment **A** is improved by functions on fragment **B**, and vice versa

**BSSE** can be *estimated* and *analysed* (a posteriori)  
via the **Counterpoise Correction**:



Lower the energy:  
**extra binding**  
between **A** and **B**

**Ghost Functions**  
BFs without atoms

\*PW are **BSSE free**  
as they always fill  
the whole box

# How to Choose a Basis Set

Balance between **Accuracy**  
and **Computational Cost**

\*computational cost should not determine what basis set is used

## Starting point:

### Molecular basis sets

- Well defined
- Hierarchy
- Databases



Usually require **modification** to be suitable for **solid-state** (especially larger BS)

**Remove more diffuse functions**  
**Screening for LD** (LDREMO keyword)

## Solid-state basis sets

- Larger variety of binding  
→ basis sets are less transferable
- **All-purpose** vs **system-specific** optimized basis sets
- Databases

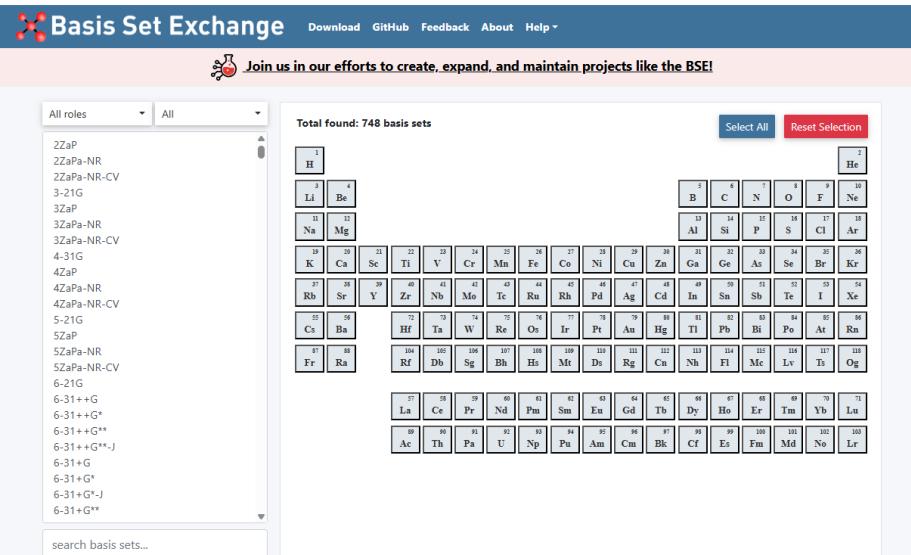
*All-purpose* **POB DZVP** and **TZVP**  
also revised version (**rev2**, less BSSE)  
Elements from H to Po  
(Bredow & co. *JCC*, 40.27 2019)

# Gaussian Basis Set Databases

## Molecular basis sets:

### Basis set exchange

[www.basissetexchange.org](http://www.basissetexchange.org)

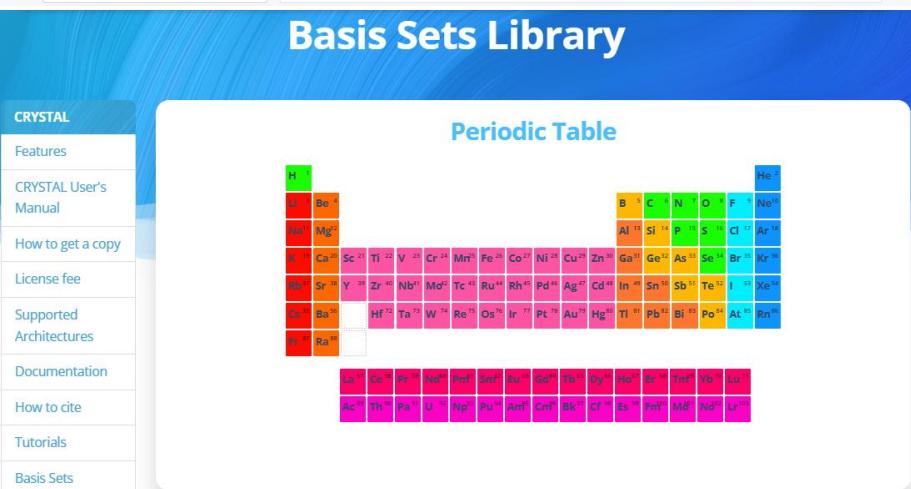


The screenshot shows the Basis Set Exchange website. At the top, there is a navigation bar with links for Download, GitHub, Feedback, About, and Help. Below the navigation bar, a message encourages users to join efforts to create, expand, and maintain projects like the BSE! The main area features a search bar labeled "search basis sets..." and a large periodic table where each element is represented by a small icon of its corresponding basis set.

## Solid-state basis sets:

### Crystal website

[www.crystal.unito.it/basis\\_sets.html](http://www.crystal.unito.it/basis_sets.html)



The screenshot shows the Crystal website. On the left, there is a sidebar menu under the heading "CRYSTAL" with options: Features, CRYSTAL User's Manual, How to get a copy (selected), License fee, Supported Architectures, Documentation, How to cite, Tutorials, and Basis Sets. The main area is titled "Basis Sets Library" and contains a "Periodic Table" where each element is represented by a small icon of its corresponding basis set.

# CRYSTAL Input (Made Simple)

**Example:** MgO STO-3G

```

12 3
 0 0 3 2. 1.
    2.992E+02  1.543E-01
    5.451E+01  5.353E-01
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8 2
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    3.804E-01  7.001E-01  3.920E-01
99 0
END

```

# CRYSTAL Input (Made Simple)

## Example: MgO STO-3G

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  5.451E+01  5.353E-01
  1.475E+01  4.446E-01
 0 1 3 8. 1.
  1.512E+01 -9.997E-02  1.559E-01
  3.514E+00  3.995E-01  6.077E-01
  1.143E+00  7.001E-01  3.920E-01
 0 1 3 2. 1.
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  1.524E-01  9.004E-01  4.620E-01
8 2
 0 0 3 2. 1.
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  2.381E+01  5.353E-01
  6.444E+00  4.446E-01
 0 1 3 6. 1.
  5.033E+00 -9.997E-02  1.559E-01
  1.170E+00  3.995E-01  6.077E-01
  3.804E-01  7.001E-01  3.920E-01
99 0
END

```

```

MgO Fm-3m
 0 0 0
 225
 4.21
 2
 12 0.0 0.0 0.0
 8 0.5 0.5 0.5
BASISSET
STO-3G
SHRINK
8 8
END

```

Available **internal** Basis sets:

- STO-3G
- STO-6G
- POB-DZVP
- POB-DZVPP
- POB-TZVP
- POB-DZVP-REV2
- POB-TZVP-REV2



# Effective Core Potentials (ECP)

For **heavy elements**, core electrons:

- Do not participate much in bonding
- Are very expensive to treat explicitly
- Are strongly relativistic



Don't need to treat them explicitly

**Effective Potential**  
Describe nucleus and inner electrons

- **Shape-consistent:**

Valence orbitals + ECP have same shape as all-electron

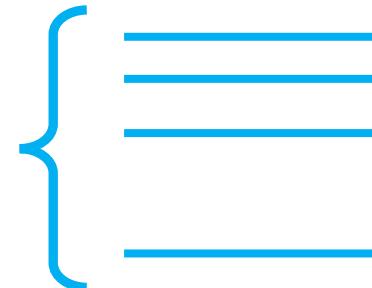
- **Energy-consistent:**

Energies of atoms computed with the ECP match all-electron

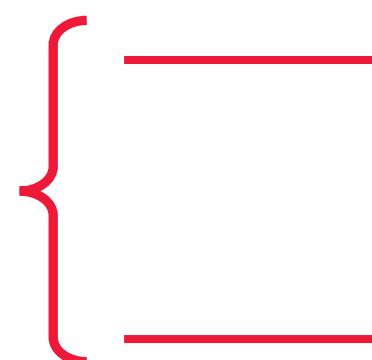
- **Relativistic Effects:**

Can be included in the ECP, at different levels of approximations

VALENCE  
BS



CORE  
ECP



# Library of ECPs

**Stuttgart/Cologne** energy-consistent (ab initio) pseudopotentials

[www.tc.uni-koeln.de/PP/index.en.html](http://www.tc.uni-koeln.de/PP/index.en.html)

Available in CRYSTAL format

Labelled as: **ECPnXY**

**n** = nr. of core electrons

**XY** = type of fit and relativistic

**Example:** ECP10MWB

- Nucleus +  $1s_2 2s_2 2p_6$  replaced by ECP (10 e<sup>-</sup>)
- Multi-valence-electron atom used in fit (M)
- Relativistic (WB)

## Energy-consistent Pseudopotentials of the Stuttgart/Cologne Group

Chose the data format and click an element in the periodic table to get the pseudopotential parameters and corresponding optimized valence basis sets !

Data format:

Crystal09

Periodic system of elements:

H	Click on the element for which you want a pseudopotential and a basis set !																		He
Li	Be																		
Na	Mg																		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	Ln	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	An	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Ut	Fl	Up	Lv	Us	Uo		
Un	Ux																		
Ln=	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
An=	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	No	Lr					

# Example of ECP: ECP28WB for Sr

```

238 10
INPUT
10. 0 2 2 2 1 0
7.400074 135.479430 0
3.606379 17.534463 0
6.484868 88.359709 0
3.288053 15.394372 0
4.622841 29.888987 0
2.246904 6.659414 0
4.633975 -15.805992 0
0 0 3 2. 1
 5.8791570 0.1967090
 3.0924820 -0.6258980
 0.6446670 0.7357230
0 0 1 2. 1
 0.2988760 1.0
0 0 1 0. 1
 0.0572760 1.0
0 0 1 0. 1
 0.0238700 1.0
0 2 3 6. 1
 2.4324720 -0.3748990
 1.6642340 0.3876150
 0.5699890 0.6558380
0 2 1 0. 1
 0.2207180 1.0
...

```

Core:  $1s_2 2s_2 2p_6 3s_2 3p_6 3d_{10}$   
**28 electrons in core**  
**10 valence electrons**

# Example of ECP: ECP28WB for Sr

```

238 10
INPUT
10. 0 2 2 2 1 0
7.400074 135.479430 0
3.606379 17.534463 0
6.484868 88.359709 0
3.288053 15.394372 0
4.622841 29.888987 0
2.246904 6.659414 0
4.633975 -15.805992 0
0 0 3 2. 1
      5.8791570 0.1967090
      3.0924820 -0.6258980
      0.6446670 0.7357230
0 0 1 2. 1
      0.2988760 1.0
0 0 1 0. 1
      0.0572760 1.0
0 0 1 0. 1
      0.0238700 1.0
0 2 3 6. 1
      2.4324720 -0.3748990
      1.6642340 0.3876150
      0.5699890 0.6558380
0 2 1 0. 1
      0.2207180 1.0
...

```

Core:  $1s_2 2s_2 2p_6 3s_2 3p_6 3d_{10}$   
**28 electrons in core**  
**10 valence electrons**

Can be simple

```

238 10
STUTSC
0 0 3 2. 1
      5.8791570 0.1967090
      3.0924820 -0.6258980
      0.6446670 0.7357230
0 0 1 2. 1
      0.2988760 1.0
0 0 1 0. 1
      0.0572760 1.0
0 0 1 0. 1
      0.0238700 1.0
0 2 3 6. 1
      2.4324720 -0.3748990
      1.6642340 0.3876150
      0.5699890 0.6558380
0 2 1 0. 1
      0.2207180 1.0
...

```

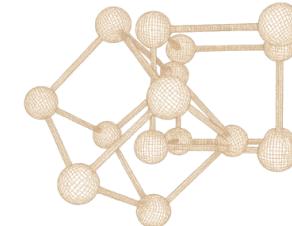
## Internal ECPs Libraries

Refer to user manual for  
list of libs and atoms

# Final Remarks

- The ultimate **accuracy** of any calculation is determined by the **basis set** used
- **Libraries** of basis sets are best starting point
- Molecular (or new) basis sets may need to be **modified** (or re-optimized)
- Basis set must have sufficient **flexibility**
  - Need to consider:
    - **Number** and **type of functions** per shell
    - **Number of shells** per atom/ion
- **Care needed** to achieve **convergence** of quantity of interest
  - Some properties are easier than others
  - Try to use a hierarchy of BS (DZ, TZ, ...)

# Acknowledgment



Advanced School on  
**QUANTUM MODELLING**  
of Materials with CRYSTAL



UNIVERSITÀ  
DI TORINO

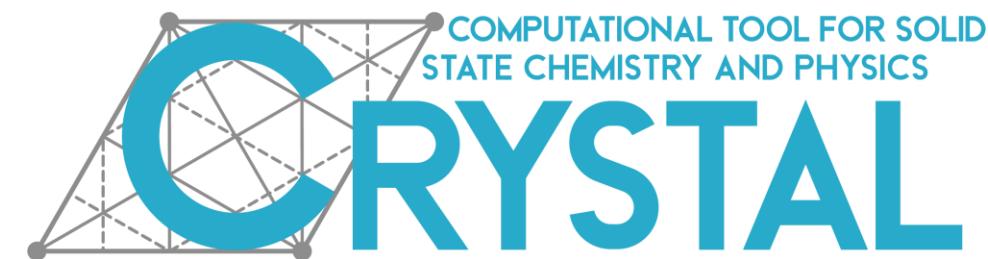


2023 - 2027

DIPARTIMENTO  
DI ECCELLENZA  
Ministero dell'Università e della Ricerca



The material presented has been adapted from slides  
kindly provided by Prof. **Bartolomeo Civalleri**



COMPUTATIONAL TOOL FOR SOLID  
STATE CHEMISTRY AND PHYSICS