

Advanced School on
QUANTUM MODELLING
of Materials with CRYSTAL



UNIVERSITÀ
DI TORINO

Local Gaussian-Type Basis Functions for Solids

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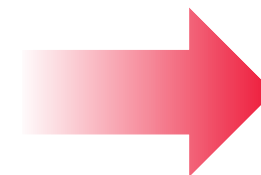
Outline

- 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⁻

Approximations

Hartree-Fock

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

KS-DFT

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

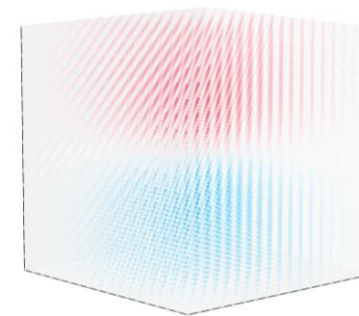
In both, we need to describe
the **single-particle orbital**

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

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

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

Size of Basis Set $\rightarrow N_{\text{BS}}$

Coefficients (unknown) $\rightarrow c_{\mu i}$

Basis Function (known) $\rightarrow \chi_{\mu}(\mathbf{r})$

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

Matrix Equation

$$\mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E}$$

Hamiltonian Matrix $\mathbf{H} \rightarrow H_{\mu\nu} = \langle \chi_{\mu} | H_i | \chi_{\nu} \rangle$

Overlap Matrix $\mathbf{S} \rightarrow S_{\mu\nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle$

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

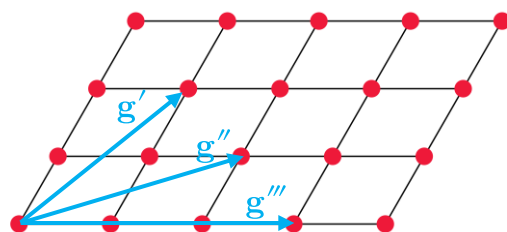
Infinite Periodic Systems \longrightarrow Translational Symmetry in Potential

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

Bravais Lattice

Vectors

Point to any cell in
the lattice



The only solution is:

Bloch's Theorem

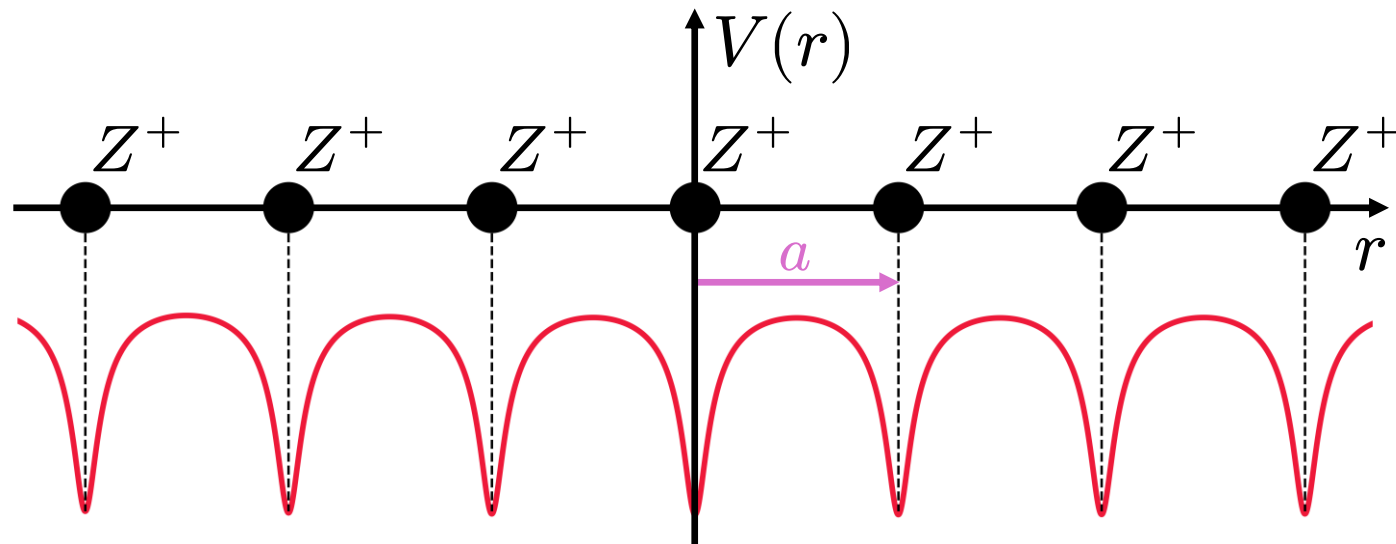
$$\psi_i^{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}}$$

Phase Factor

Periodic

(describes only unit cell)

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{g})$$



\longrightarrow Plane Waves

\longrightarrow Localized Functions

Plane Waves

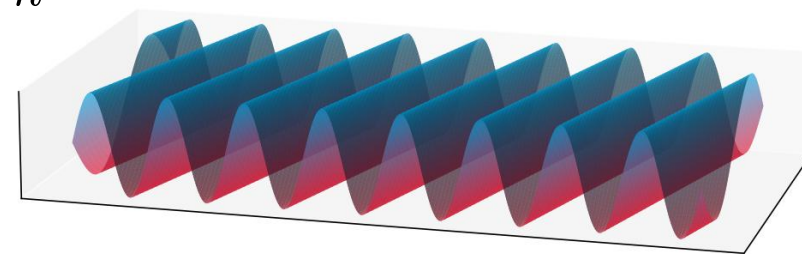
Bloch's Theorem $\psi_i^{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}$

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

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\boldsymbol{\kappa}} c_{i\mathbf{k}}(\boldsymbol{\kappa}) e^{i\boldsymbol{\kappa}\cdot\mathbf{r}}$$

And combining with Bloch's Theorem we get:

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



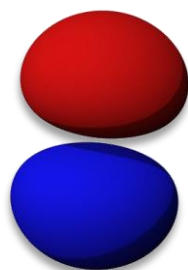
1. Inherently **Bloch Functions**
2. **Orthogonal**
3. Number of PW (basis set quality)
controlled by a single **energy cutoff**
→ systematic improvement
4. **Difficult** describe the **electronic structure** near nuclei
→ **Pseudopotentials** must be used

$$\psi_i^{\mathbf{k}}(\mathbf{r}) = \sum_{\boldsymbol{\kappa}}^{\frac{1}{2}|\mathbf{k}+\boldsymbol{\kappa}|^2 \leq E_{\text{cut}}} c_{i\mathbf{k}}(\boldsymbol{\kappa}) e^{-i(\boldsymbol{\kappa}+\mathbf{k})\cdot\mathbf{r}}$$

Examples:
Quantum ESPRESSO,
VASP, CASTEP

Localized Functions

$\chi_\mu(\mathbf{r})$
Localized Function
Atomic Orbital



FT

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

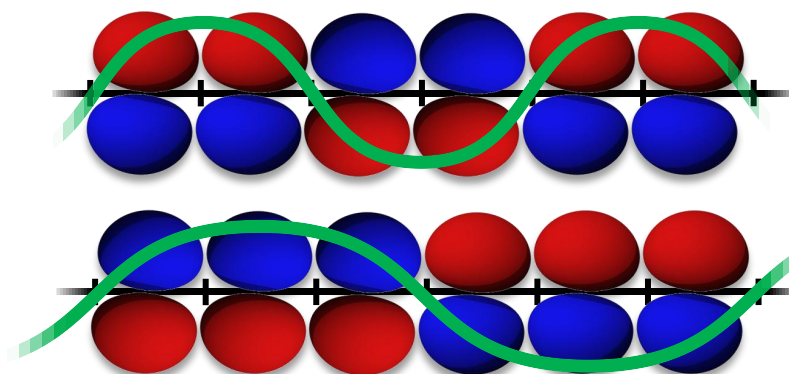
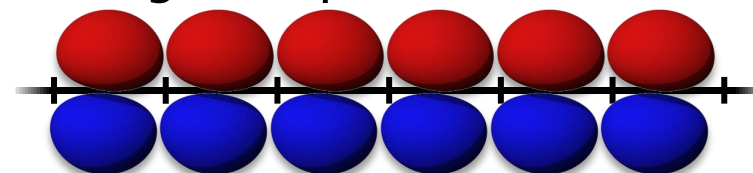
Bloch Function
Periodic

Lattice Vectors
Atomic Position

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

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

Reproduce $\chi_\mu(\mathbf{r})$ orbital
along each periodic direction

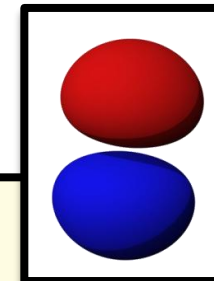


$k = 2$
 $e^{-i\mathbf{k} \cdot \mathbf{g}}$
Phase Factor

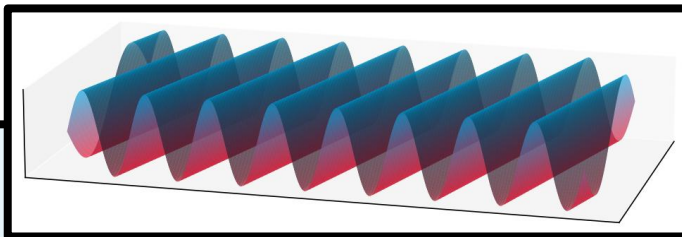
$k = 3$
Example:
CRYSTAL

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



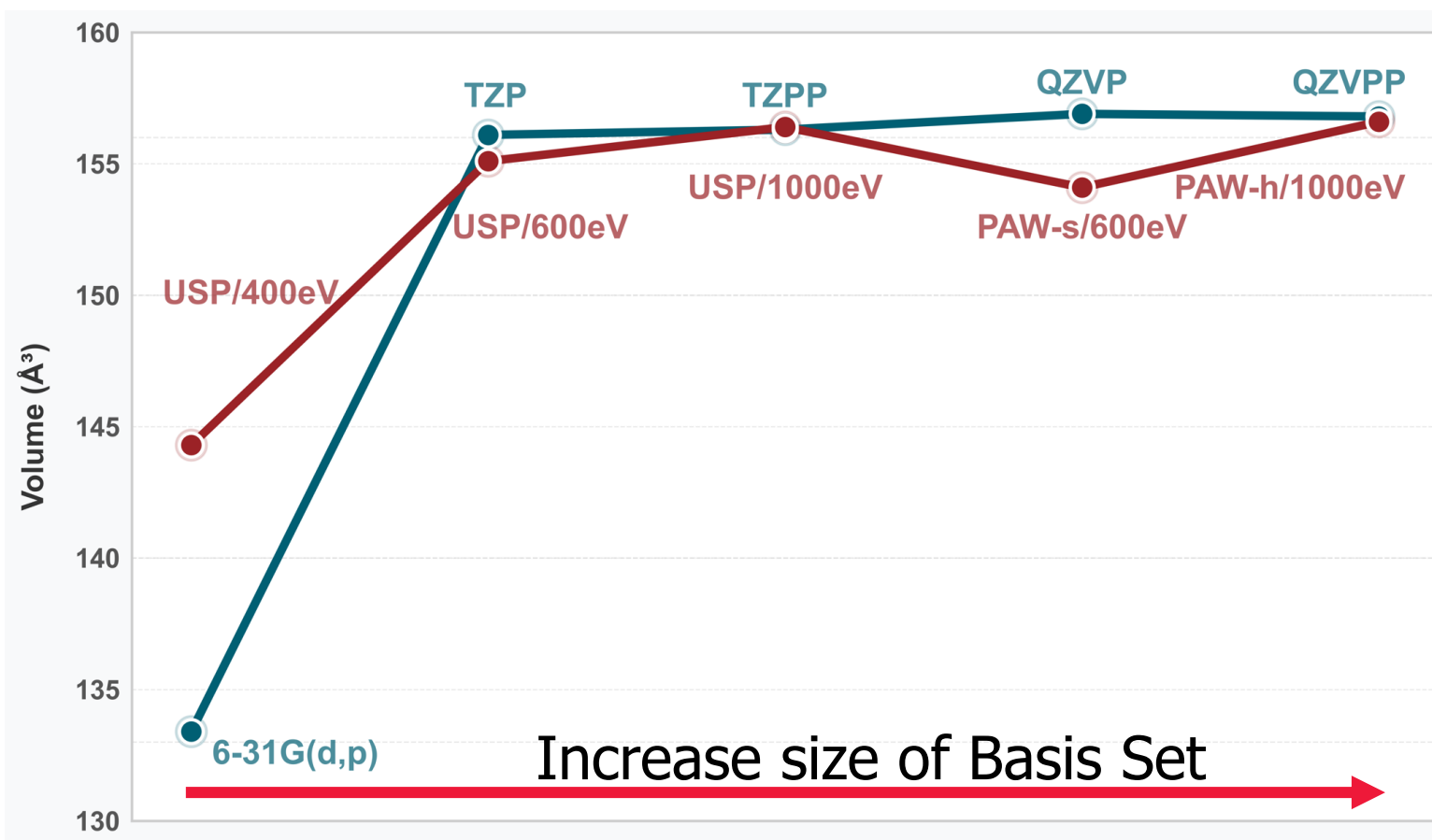
- **Universal**
- **Need Pseudopotentials**
- Large number of PWs needed
- **Non Local**
→ **Loss of chemical insight**
- **Systematic improvements**
(with E_{cut})
- Numerical efficient
- **3D periodic replicas for 2D, 1D and molecules**
- **No basis set Superposition Error**
- **Expensive hybrid calculations**

Local BS

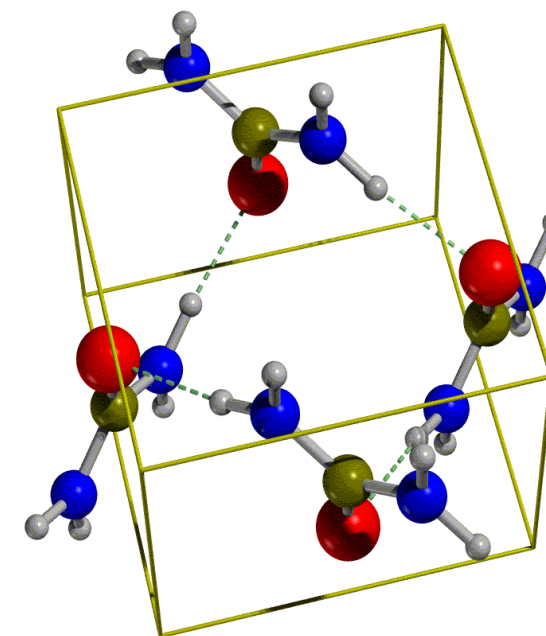
- **Element Specific**
- **All-electron** and Pseudopotentials
- Small Basis Set can give accurate results
- **Local**
→ **Chemical insight is given**
- **Systematic improvement not easy**
- Computational efficient
- **No artificial replica for 2D, 1D and molecules**
- **Basis Set Errors**
- **Efficient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

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

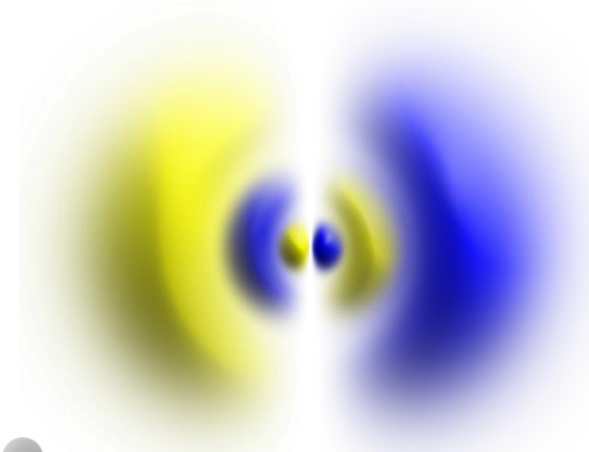
Radial Function

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

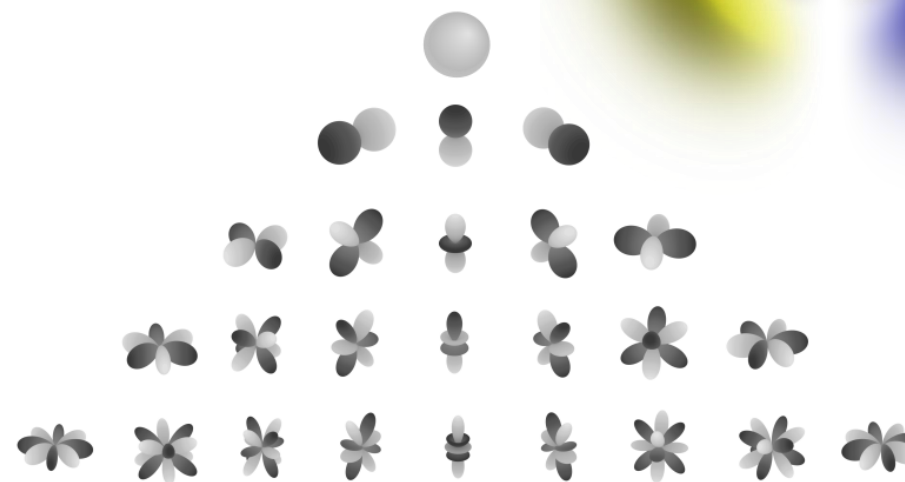
Angular Function

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

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)

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

Hydrogen Orbital like behaviour:

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

Gaussian-Type Orbital (GTO)

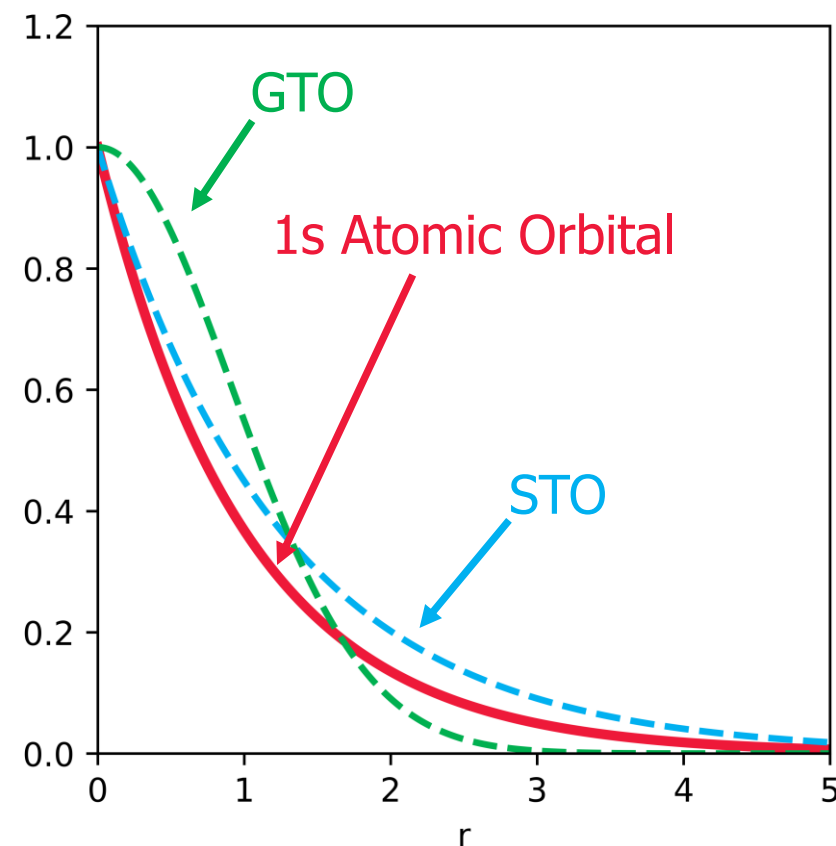
$$R_{nl}^{\text{GTO}}(r) = N_{nl} r^{2n-1} e^{-\alpha r^2}$$

Wrong behaviour:

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

→ product of two gaussians is still a gaussian

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



Gaussian-type Basis Functions

Spherical Gaussian Functions

$$\chi_{nlm}^{\text{spher}}(r, \theta, \varphi) = N_{nlm} Y_{lm}(\theta, \varphi) r^{2n-1-2} e^{-\alpha r^2}$$

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

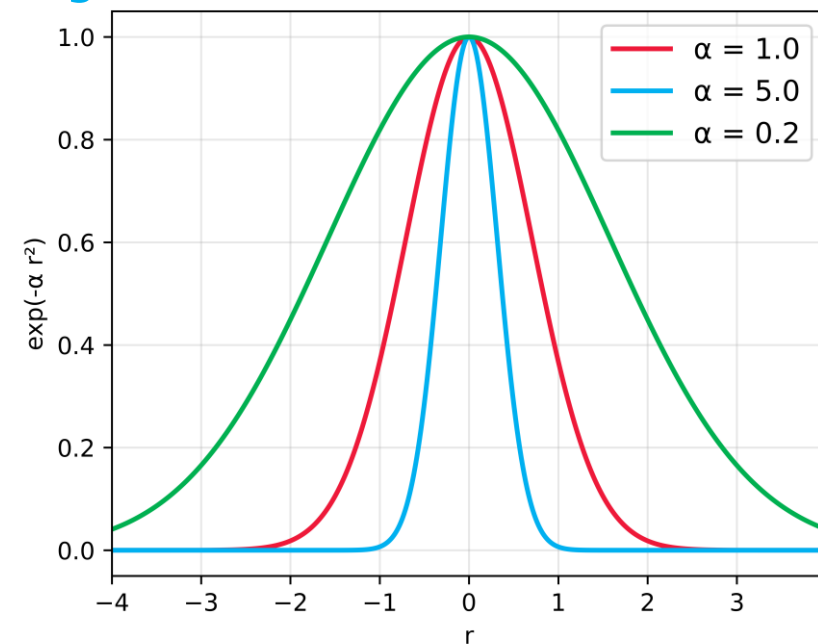
Cartesian Gaussian Functions

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

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)

α 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

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

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

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**

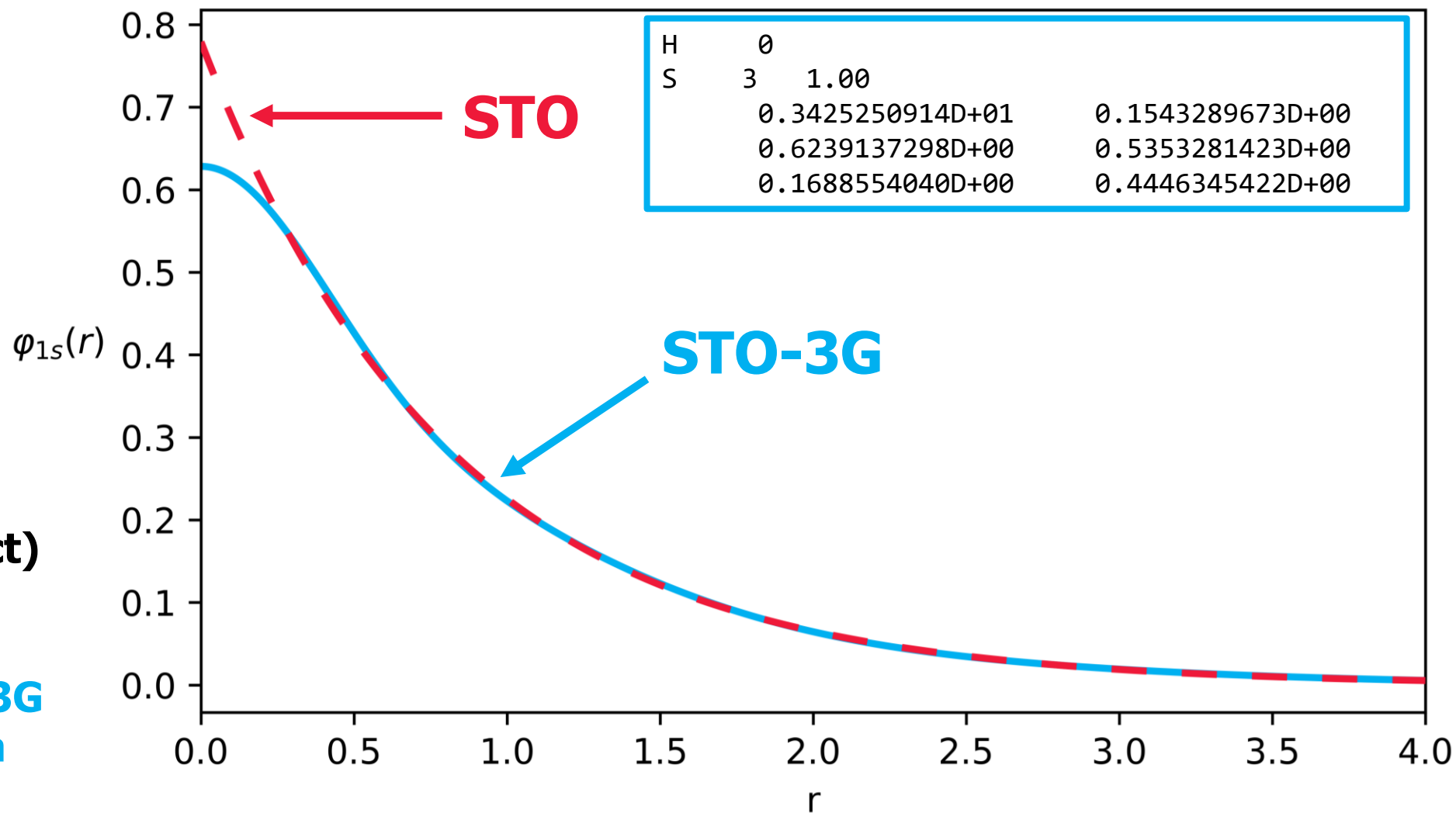
Example of Contraction

H atom, 1s Orbital

$$N_G = 3$$

Energy (exact)
-0.5 Ha

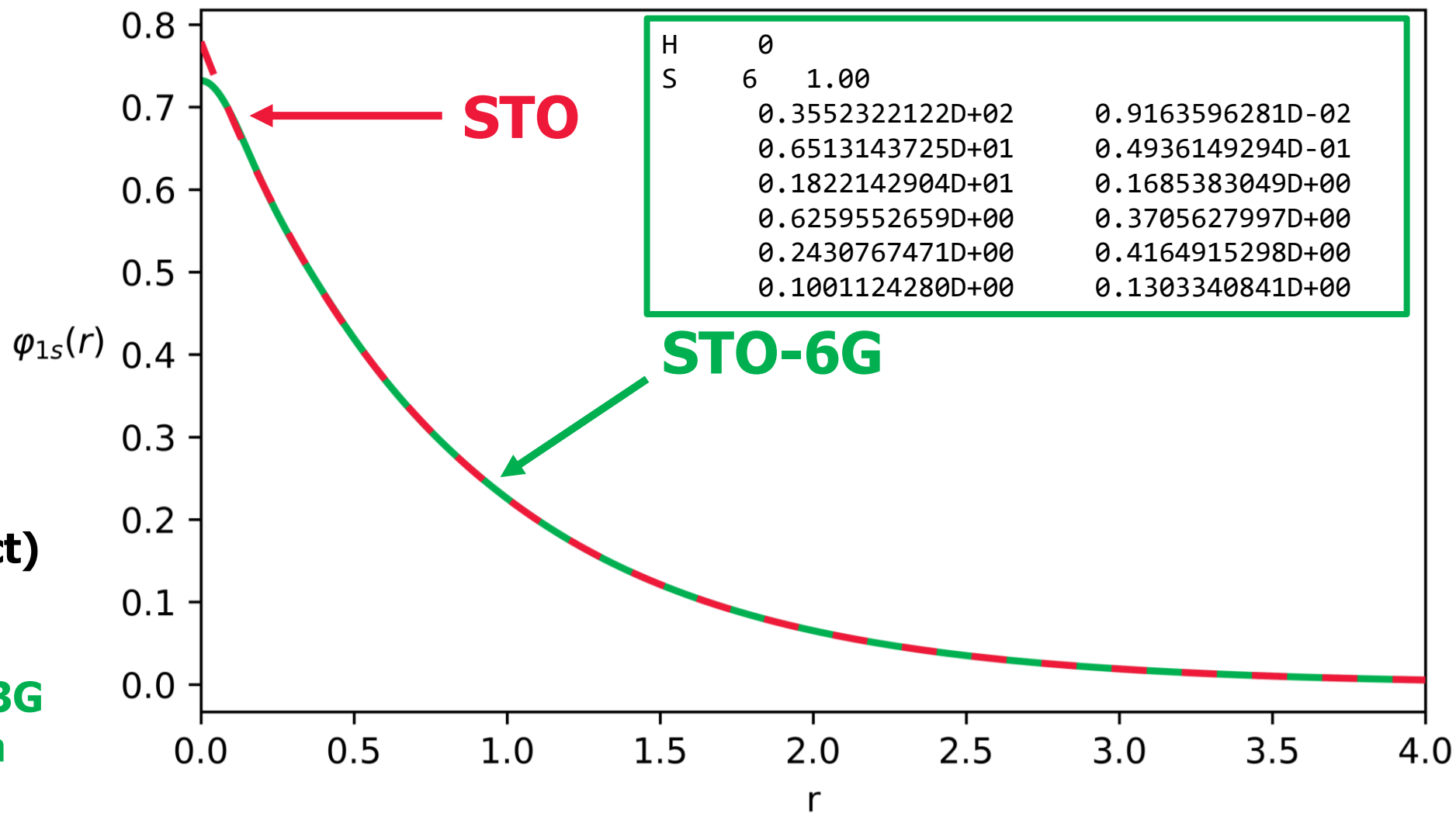
Energy STO-3G
-0.49491 Ha



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

H: 1s

C: 1s, 2s, 2p_x, 2p_y, 2p_z

Double-Zeta (**DZ**)

Two basis function for each occupied orbital

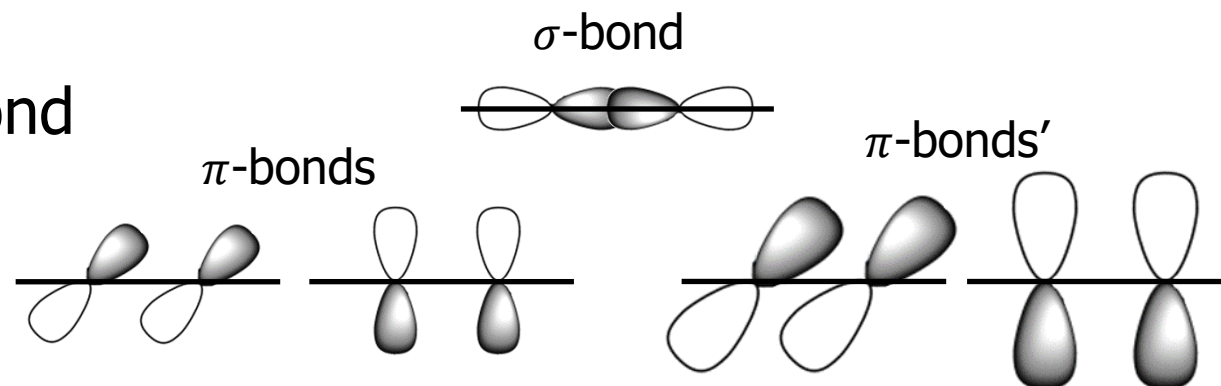
- **extend** the basis
- crucial **physical** and **chemical relevance**

H: 1s, 1s'

C: 1s, 1s', 2s, 2s', 2p_{x,y,z}, 2p_{x,y,z}'

Example: C-C Triple Bond

- Tighter 2p_z function is enough for the σ -bond
- More diffuse 2p_x and 2p_y functions are better for electron distribution of π -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: $1s, 1s', 1s'', 2s, 2s', 2s'', 2p_{x,y,z}, 2p_{x,y,z}', 2p_{x,y,z}''$

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

 How many functions do we need?

Bonding occurs between
valence electrons

VALENCE { 

CORE { 

Split-Valence (V, SV)

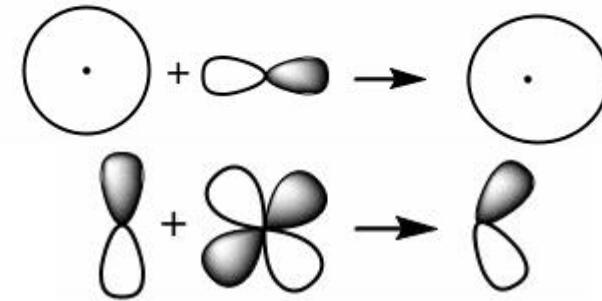
Minimal basis for core orbitals, double/triple/... basis for valence orbitals

 **DZV, TZV**, etc.

Classification of GTO Basis Sets

Polarization Functions (**P**)

Angular momentum not occupied in the atom



Example:

- H, He: occ. **s**-orbitals \longrightarrow **p**-type functions
- 1st - 2nd rows: occ. **p**-orbitals \longrightarrow **d**-type functions
- TM: occ. **d**-orbitals \longrightarrow **f**-type functions
- Lanthanides: occ. **f**-orbitals \longrightarrow **g**-type functions

Available since

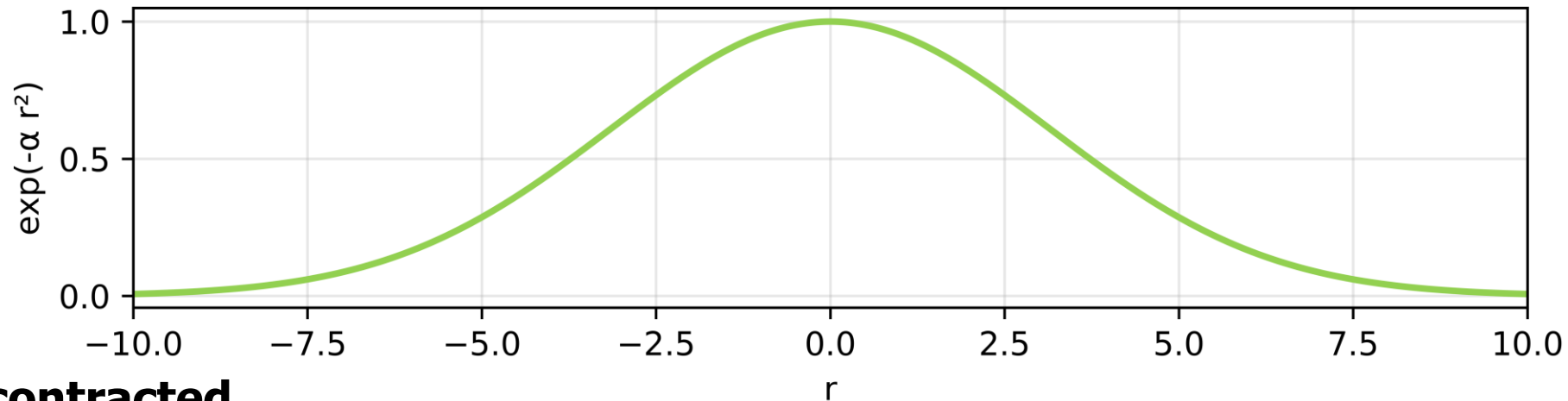

Important to describe polarized electronic charge distributions (ECD) (e.g. **polar bonds**)
dipole moment, polarizability, dielectric response, anisotropy of ECD upon **cell deformation, H-bonding**, correlation energy

\longrightarrow **DZVP, TZVP**, etc.

Classification of GTO Basis Sets

Diffuse Functions (+, D, aug-)

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



Usually **uncontracted**

Useful to describe 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 \longrightarrow 3 s contracted func.
- 4 p primitives \longrightarrow 2 p contracted func.

In addition:

{Contraction scheme}

Example: {631/31}

- 3 s contracted func. \longrightarrow 6 G 3 G 1G
- 2 p contracted func. \longrightarrow 3 G 1 G

Quality	Label	Name
SZ	Pople	STO-3G
DZ	Pople	3-21G
DZP	Jensen	pc-0
	Pople	6-31G*
	Ahlrichs	Def2-SV(P)
	Ahlrichs	Def2-SVP
	Jorge	DZP
	Sapporo	DZP
	Roos	ANO-DZP
	Dunning	cc-pVDZ ¹
	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
QZP	Ahlrichs	Def2-QZVPP
	Sapporo	QZP
	Roos	ANO-QZP
	Dunning	cc-pVQZ
	Jensen	pc-3
5ZP	Dunning	cc-pV5Z
	Jensen	pc-4

Examples of common families of *molecular* BSs

Usually, BSs are known *by their names*

CRYSTAL Input

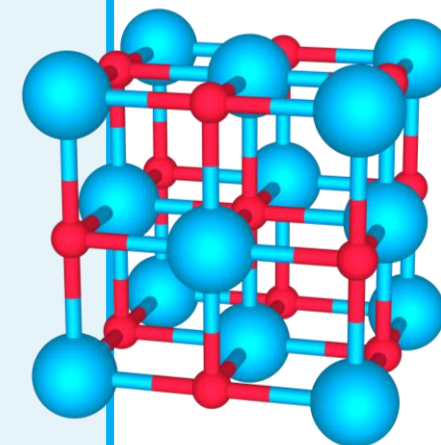
Example: MgO STO-3G

```

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
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  2.381E+01 5.353E-01
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  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

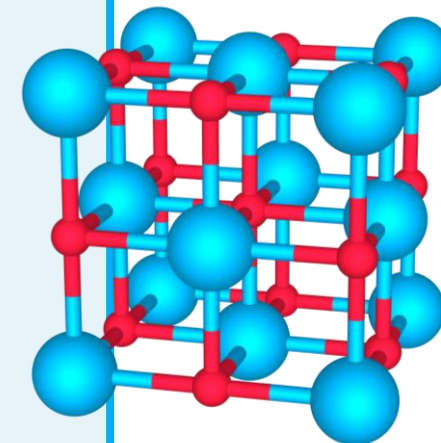


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Example: MgO STO-3G

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99 0
END
```

Atomic Number Number of Shells
Custom BS Input



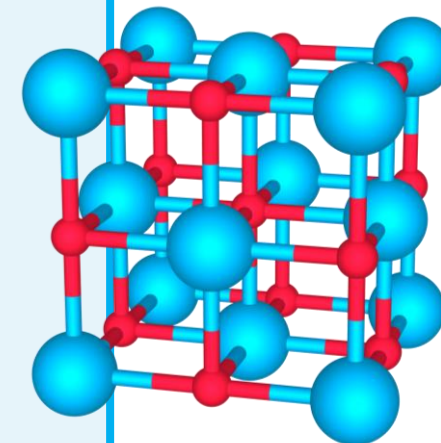
CRYSTAL Input

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  1.143E+00  7.001E-01  3.920E-01
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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	0	s
	1	sp
	2	p
	3	d
	4	f
	5	g



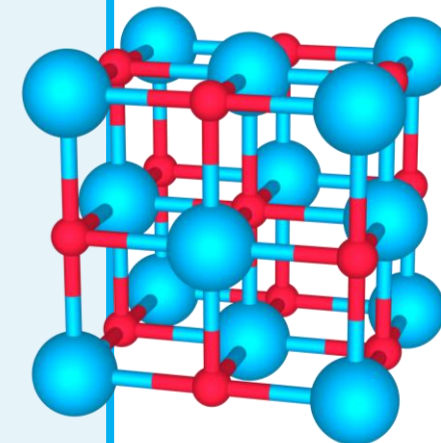
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Example: MgO STO-3G

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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



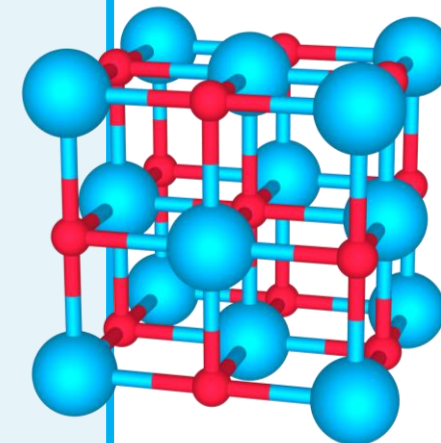
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1.143E+00 7.001E-01 3.920E-01
0 1 3 2. 1.
1.395E+00 -2.196E-01 1.059E-02
3.893E-01 2.256E-01 5.952E-01
1.524E-01 9.004E-01 4.620E-01
8 2
0 0 3 2. 1.
1.307E+02 1.543E-01
2.381E+01 5.353E-01
6.444E+00 4.446E-01
0 1 3 6. 1.
5.033E+00 -9.997E-02 1.559E-01
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)



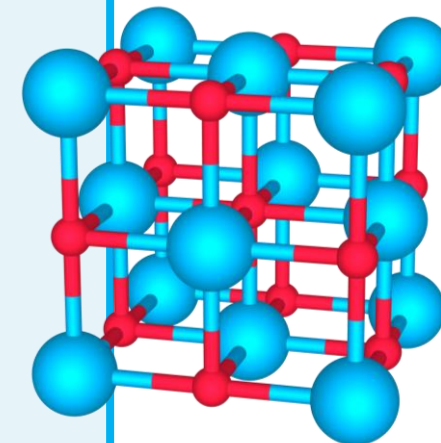
CRYSTAL Input

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
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



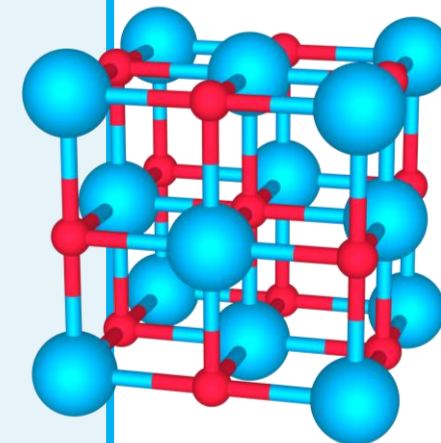
CRYSTAL Input

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

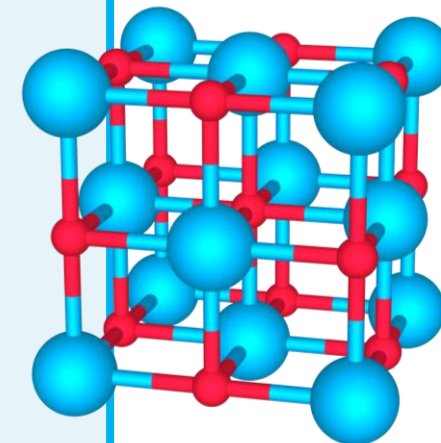
```

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.
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
    
```

Annotations in the input file:

- Shell sp**: Points to the first shell (0 1 3 8. 1.)
- s**: Points to the second shell (0 1 3 2. 1.)
- p**: Points to the third shell (0 1 3 6. 1.)

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



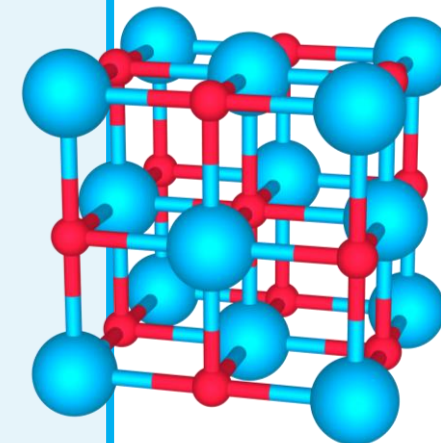
CRYSTAL Input

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.
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

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 \longrightarrow too many basis functions

Complete Basis Set (CBS) limit \longrightarrow **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:

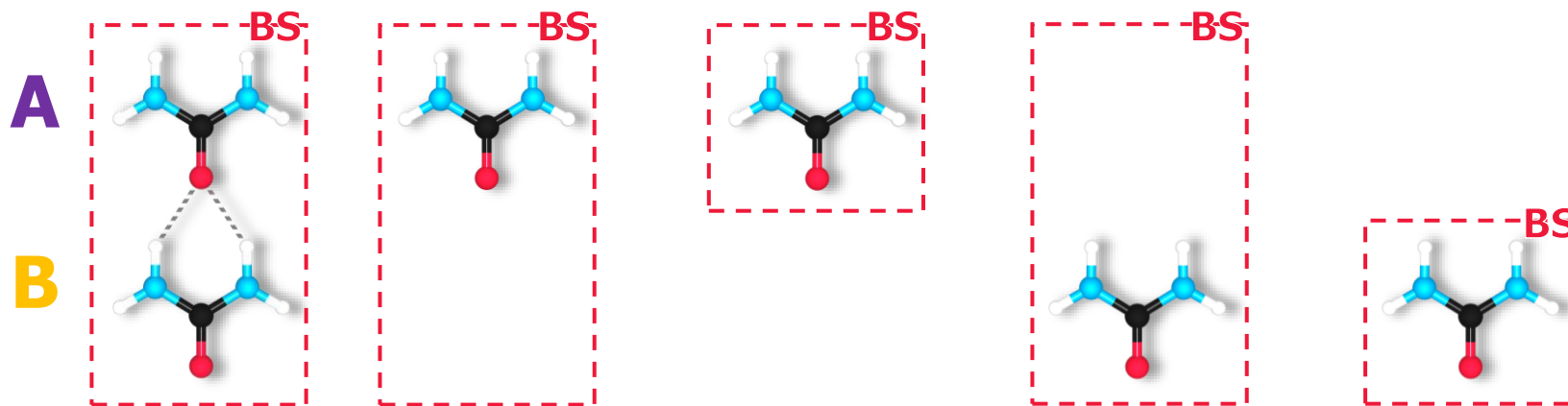
→ Description of fragment **A** is improved by functions on fragment **B**, and vice versa

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



$$E_{AB}^{\text{CP}} = E_{AB} - \underbrace{[E_A(AB) - E_A(A)]}_{E_A^{\text{BSSE}}} - \underbrace{[E_B(AB) - E_B(B)]}_{E_B^{\text{BSSE}}}$$

**Total
Corrected Energy**

***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

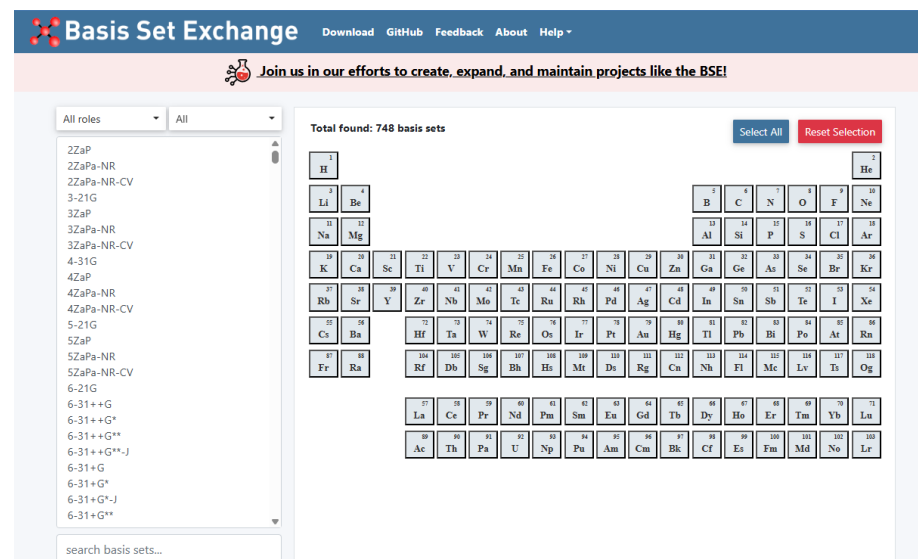
All-purpose **POB DZVP** and **TZVP**
also revised version (**rev2**, less BSSE)
Elements from H to Po
(Bredow & co. *JCC*, 40.27 2019)

Gaussian Basis Set Databases

Molecular basis sets:

Basis set exchange

www.basissetexchange.org

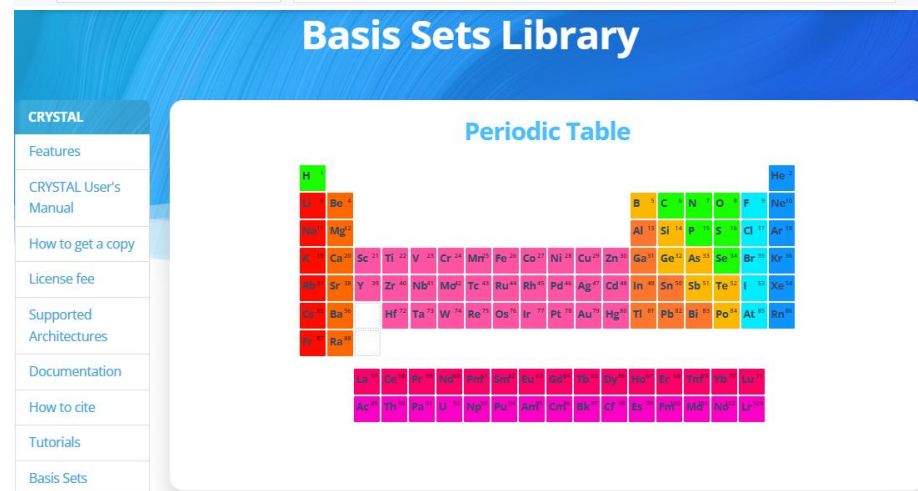


The screenshot shows the Basis Set Exchange (BSE) website interface. At the top, there's a navigation bar with links for Download, GitHub, Feedback, About, and Help. Below this, a banner encourages users to join efforts to create, expand, and maintain projects like the BSE. The main content area displays a list of basis sets on the left, categorized by 'All roles' and 'All'. The list includes various molecular basis sets such as 22aP, 22aPa-NR, 3-21G, 32aP, 32aPa-NR, 32aPa-NR-CV, 4-31G, 42aP, 42aPa-NR, 42aPa-NR-CV, 5-21G, 52aP, 52aPa-NR, 52aPa-NR-CV, 6-21G, 6-31++G, 6-31++G*, 6-31++G***, 6-31++G***, 6-31+G, 6-31+G*, 6-31+G*-J, and 6-31+G**. On the right, a periodic table is shown with elements color-coded by their associated basis sets. A search bar at the bottom left allows users to search for specific basis sets.

Solid-state basis sets:

Crystal website

www.crystal.unito.it/basis_sets.html



The screenshot shows the 'Basis Sets Library' section of the Crystal website. It features a sidebar with a list of links: Features, CRYSTAL User's Manual, How to get a copy, License fee, Supported Architectures, Documentation, How to cite, Tutorials, and Basis Sets. The main content area displays a periodic table with elements color-coded by their associated basis sets. The table is titled 'Periodic Table' and shows elements from Hydrogen (H) to Oganesson (Og). The color-coding indicates different basis set families, such as 22aP (red), 3-21G (orange), 32aP (yellow), 32aPa-NR (green), 4-31G (blue), 42aP (purple), 42aPa-NR (pink), 5-21G (brown), 52aP (grey), 52aPa-NR (light blue), 6-21G (light green), 6-31++G (light orange), 6-31++G* (light yellow), 6-31++G*** (light pink), 6-31+G (light blue), 6-31+G* (light green), 6-31+G*-J (light orange), and 6-31+G** (light purple).

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
    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
```

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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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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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:

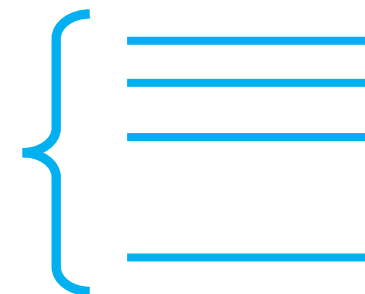
- Do not participate much in bonding
- Are very expensive to treat explicitly
- Are strongly relativistic

Don't need to treat
them explicitly

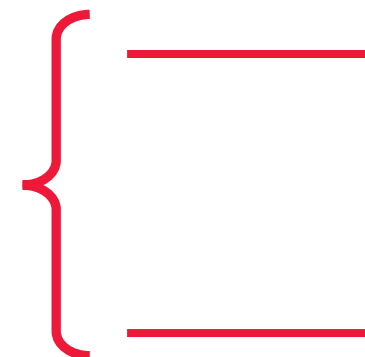
Effective Potential

Describe nucleus and inner
electrons

VALENCE
BS



CORE
ECP



- **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

Library of ECPs

Stuttgart/Cologne energy-consistent (ab initio) pseudopotentials

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^-)
- 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:

Periodic system of elements:

H	Click on the element for which you want a pseudopotential and a basis set !																He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
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	Uu	Fl	Up	Lv	Us	Uu
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	Md	No	Lr		

Example of ECP: ECP28MWB 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: ECP28MWB 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
...
```

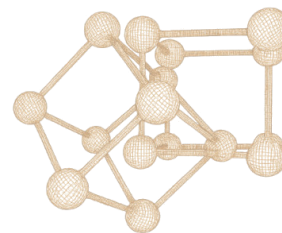
Internal ECPs
Libraries

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



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

