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# Examples of Basis Sets

## *References and Acknowledgements*

*The material discussed here is following the textbook below. These notes will be enhanced later in the course after we cover DFT methods*

- [Methods of Electronic structure calculations: From molecules to solids](#),  
M. Springborg (Chapter 10)

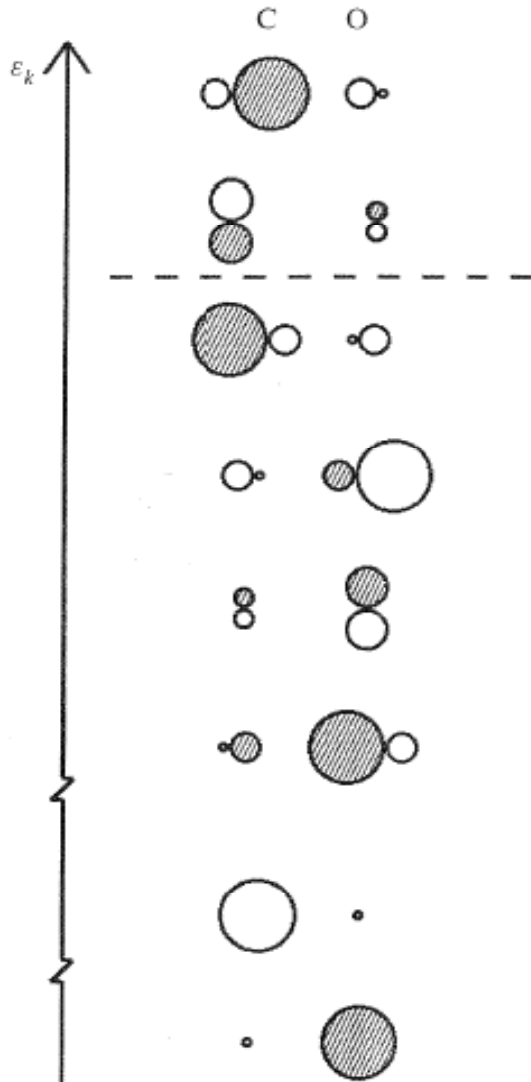
# Roothaan's approach: selecting the basis

- In the Hartree-Fock approach we approximated the  $N$ -electron wavefunction  $\Psi_e$  with a single Slater determinant  $\Phi$ , containing  $N$  single-electron orbitals  $\phi_k$ .
- The Hartree-Fock equations should be solved to determine  $\phi_k$  and the single-particle energies  $\varepsilon_k$ .
- In Roothaan's approach, to make the calculations possible for realistic systems, the orbitals are expanded in a set of pre-defined basis functions  $X_i$ .

$$\phi_k(\vec{x}) = \sum_{i=1}^{N_b} X_i(\vec{x}) c_{ik}$$

- **How do the basis functions  $X_i$  are chosen? One may be guided by physical intuition.**

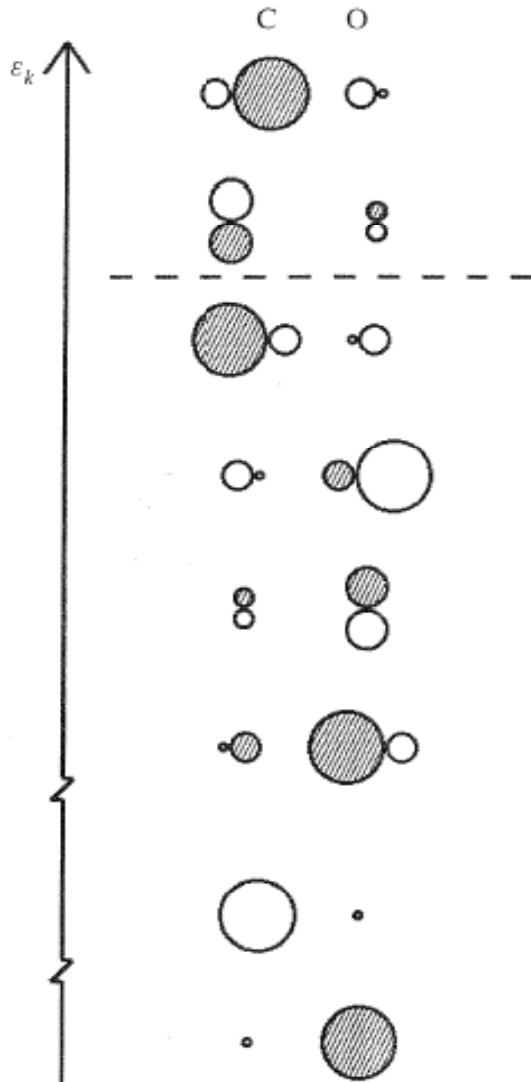
# Selecting the basis functions



From [M. Springborg](#)

- ▶ A schematic is shown of what we could expect in a CO molecule.
- ▶ For the isolated C and O atoms we have 1s, 2s, and 2p electrons, and we will expect that the molecular orbitals are formed from these functions.
- ▶ O has larger nuclear charge than C. Thus equivalent orbitals of the isolated C and O atoms will have lower energies for O than for C.

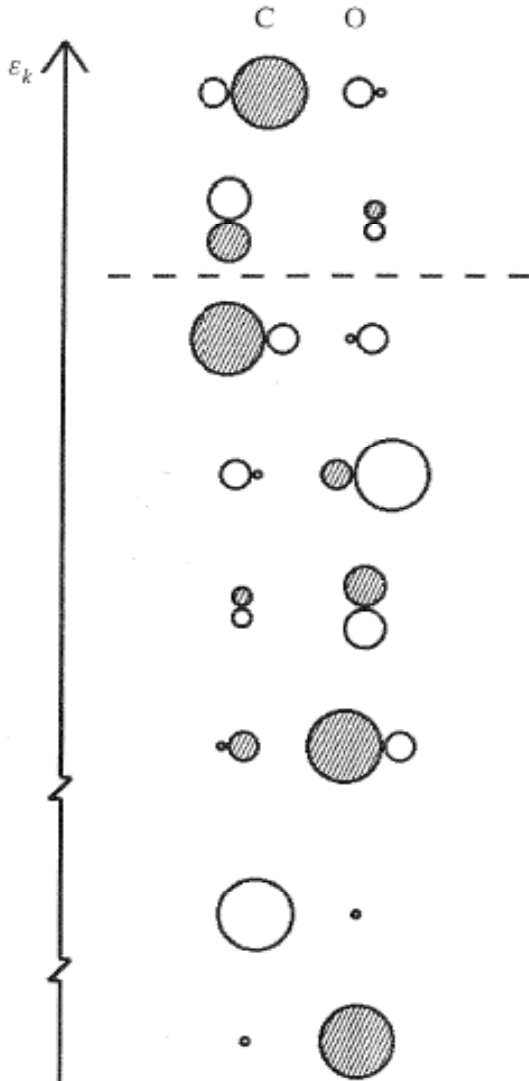
# Selecting the basis functions



- The atomic 1s orbitals are localized in space and don't interact in the molecule. Thus, the two lowest molecular orbitals will be basically pure atomic 1s orbitals.
- The situation is different for the valence electrons. sp hybrids from the atomic 2s and 2p functions, lead to atomic orbitals that point from one atom towards the other or away from it.
- The bonding combination of these that point towards each other will lead to a very strongly bonding orbital with the lower energy above those of the 1s orbitals, whereas the corresponding antibonding combination will have higher energy.

From [M. Springborg](#)

# Selecting the basis functions



- ▶ In between those, we have the bonding combinations of the  $sp$  hybrids pointing away from the other atom, as well as the bonding combination of the  $p$  orbitals perpendicular to the molecular axis (the later will be fourfold degenerate when including spin).
- ▶ We will also have at higher energies the corresponding antibonding combinations in the reverse order.

From [M. Springborg](#)

# Using atomic orbitals

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- Thus the picture based on constructing molecular orbitals from atomic functions seems to be adequate.
- Therefore, a very useful set of basis functions is one consisting of atomic orbitals. Thus, we may choose

$$\chi(\vec{r}) = R_{nl}(r)Y_{lm}(\theta, \phi).$$

- Here we have omitted the index on  $X$ , assumed that the  $X$  belongs to an atom placed at the origin, and let  $Y_{lm}$  be a spherical harmonic function.
- For an atom at another position,  $r$ ,  $\theta$  and  $\phi$ , will be the spherical coordinates with respect to that position.

# Using atomic orbitals

- How to choose the radial part  $R_{nl}$  of X?
- A simple solution will be to use the values computed numerically for the isolated atoms (even though they will change when passing to the molecule)
- On the other hand, for hydrogen-atom-like ions,  $R_{nl}$  is given as an (associated Laguerre) polynomial times an exponentially decaying function. This suggests using functions of the form:

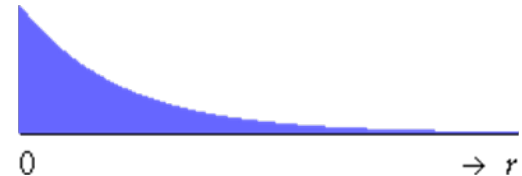
$$\chi(\vec{r}) = \chi_{R,\zeta,n,l,m}(\vec{r}) = \frac{(2\xi)^{n+1/2}}{(2n!)^{1/2}} r^{n-1} e^{-\xi r} Y_{lm}(\theta, \phi).$$

# Slater-type orbitals (STO)

- They are inspired by the wave functions of the H-atom: they are products of a radial function and a spherical harmonic.
- For the case of the H-atom, the radial part is the product of a polynome and an exponential term.
- The difference from the H-atom is the radial part which here for the Slater-type orbitals uses a product of an exponential term and a monome:

$$X = N r^q \cdot e^{-\zeta r} Y_{l,m}(\theta, \phi)$$

- **Slater-type orbitals thus do not have nodal spheres.** If wave functions have to exhibit such a characteristic (like the 2s or 3s orbital of the H-atom), they have to get it from different STOs via suitable MO-coefficients.
- The exponential term is always of the form  $e^{-\zeta r}$  as shown in the figure:



# Slater-type orbitals (STO)

$$\chi(\vec{r}) = \chi_{\bar{R},\zeta,n,l,m}(\vec{r}) = \frac{(2\zeta)^{n+1/2}}{(2n!)^{1/2}} r^{n-1} e^{-\zeta r} Y_{lm}(\theta, \phi).$$

- We may have different functions for different atoms (described by  $\bar{R}$  and meaning for example C and O for the CO molecule).
- Also for the same atom and  $(n, l)$  we may have more functions differing in the decay constants  $\zeta$ . Remember that we did an example of improving the solution from the variational principle for the H-atom playing with the decay constant  $\zeta$ .
- **We may also include functions that for the isolated atoms are not occupied such as  $p$  functions for hydrogen atoms and  $d$  functions for C and O atoms.**

# Slater-type orbitals (STO)

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$$\chi(\vec{r}) = \chi_{\bar{R},\zeta,n,l,m}(\vec{r}) = \frac{(2\zeta)^{n+1/2}}{(2n!)^{1/2}} r^{n-1} e^{-\zeta r} Y_{lm}(\theta, \phi).$$

- These functions (Slater orbitals) are normalized, but not orthogonal.
- **Using these functions, it becomes prohibitively complicated to calculate the matrix elements entering the Fock matrix.**
- Although they have the advantage of describing the eigenfunctions of systems that are physically related to the one of interest (i.e., of single-electron ions), their use has been limited.

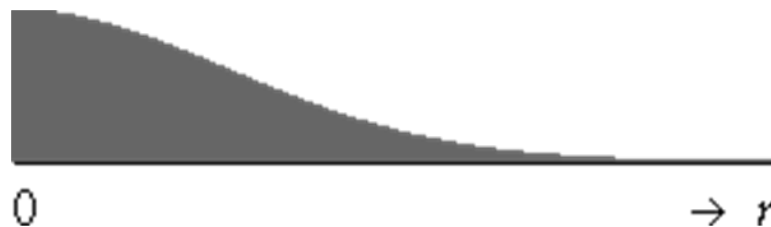
# Gaussian-type orbitals

- Can we replace the Slater-type orbitals with some functions that resembles them but for which the matrix elements of the Fock operator can be calculated easily?
- The standard solution is to use Gaussian-type orbitals (Gaussians). These are defined as

$$\chi(\vec{r}) = \chi_{R,\alpha,n,l,m}(\vec{r}) = 2^{n+1} \frac{\alpha^{(2n+1)/4}}{[(2n-1)!!]^{1/2} (2\pi)^{1/4}} r^{n-1} e^{-\alpha r^2} Y_{lm}(\theta, \phi).$$

where  $(2n-1)!! = (2n-1) \cdot (2n-3) \cdots 1$ .

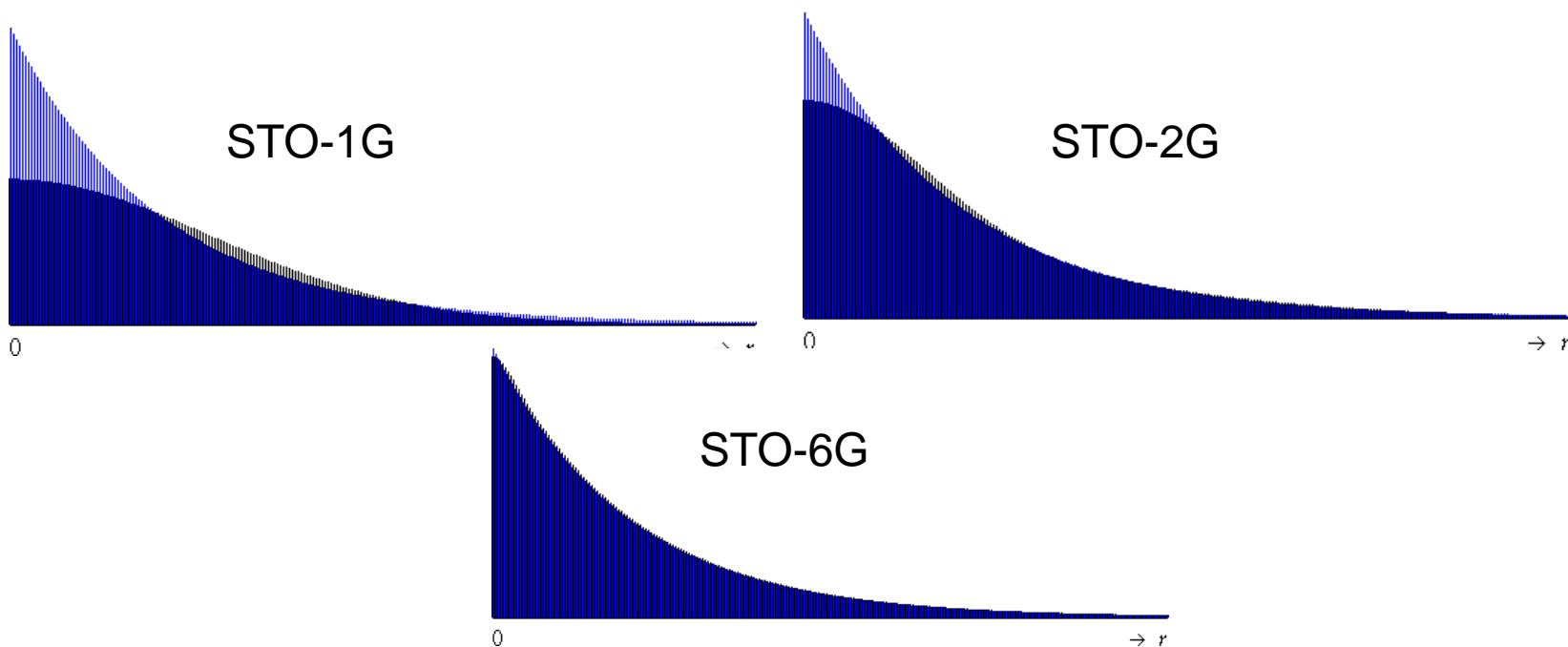
- Note that now the argument of the exponential function contains an  $r^2$  dependence instead of an  $r$  dependence.



- Due to this fact, all Gaussians have a flat tangent at the site of the nucleus.

# Gaussian-type orbitals

- Gauss-type functions are easier to integrate than Slater-type orbitals. The trade-off is that they are inferior basis functions, because of their different shape.
- A frequently used strategy uses linear combinations of Gauss-type functions. By properly choosing coefficients and exponents of these "primitive Gaussian-type functions", the characteristic of a Slater-type orbital can be reproduced quite well. Three examples are shown with 1, 2 and 6 Gaussians.



# Gaussian-type orbitals

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$$\chi(\vec{r}) = \chi_{\bar{R},\alpha,n,l,m}(\vec{r}) = 2^{n+1} \frac{\alpha^{(2n+1)/4}}{[(2n-1)!!]^{1/2} (2\pi)^{1/4}} r^{n-1} e^{-\alpha r^2} Y_{lm}(\theta, \phi).$$

- We noted that that all Gaussians have a flat tangent at the nucleus. This is not the case for e.g. for the 1s H-function.
- Since the potential diverges at the site of the nucleus, the region there is one where a large part of the total energy originates. This problem that the wave function has a wrong behavior at the site of the nucleus is a severe one (**cusp problem**).
- In order to circumvent it, one may want to use relatively many Gaussians, in particular ones with large  $\alpha$ .

# Gaussian-type orbitals

$$\chi(\vec{r}) = \chi_{\bar{R},\alpha,n,l,m}(\vec{r}) = 2^{n+1} \frac{a^{(2n+1)/4}}{[(2n-1)!!]^{1/2} (2\pi)^{1/4}} r^{n-1} e^{-ar^2} Y_{lm}(\theta, \phi).$$

- In some cases the  $Y_{lm}$  functions are replaced by simple powers of  $x/r$ ,  $y/r$ ,  $z/r$ .
- Thus, the common form of Gaussian-type functions (GTFs) becomes

$$X = N x^\alpha y^\beta z^\gamma e^{-\zeta(x^2+y^2+z^2)}$$

which can be split in a product of terms that depend only on  $x$ ,  $y$ , or  $z$ . Here,  $\alpha, \beta, \gamma = 0, 1, 2, \dots$  (1s, 2p, 3d, 4f, ...)

- This means that there will be 6  $d$ -functions.  $x^2/r^2$ ,  $y^2/r^2$ ,  $z^2/r^2$ ;  $xy/r^2$ ,  $xz/r^2$ ,  $yz/r^2$ , instead of the usual five.
- The sum of the first three forms a function of  $s$  and not  $d$  symmetry.
- Similarly, there will be ten and not seven  $f$  functions, but here one may construct three linear combinations that comprise three  $p$ -like functions.

# Polarization functions

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- **Polarization functions** are functions that exceed the angular characteristic of the highest occupied orbital of the respective atom (e.g.,  $p$ -functions for H,  $d$ -functions for C, N, O, etc.).
- The need for polarization functions can easily be seen:
  - Consider an isolated hydrogen atom has a spherical electron density, which is described perfectly by  $s$ -functions.
  - If a H-atom is placed in an electric field, the electron density is distorted in the direction of this field. A distortion of this kind cannot be described by  $s$ -functions;  $p$ -functions are needed since they have orientation build in.
  - Within a molecule, an electric field may be induced by polar chemical bonds.

# Polarization functions

- Thus more accurate results are often obtained when the basis set, as constructed from the orbitals of the isolated atoms, is augmented with polarization functions, i.e.  $p$  functions on H-atoms,  $d$  functions on atoms of the 2<sup>nd</sup> and 3<sup>rd</sup> row, etc.
- A standard notation for a Gaussian basis set would be e.g. (8,4,1) for the carbon atom:
  - ✓ eight Gaussians of  $s$  symmetry,
  - ✓ four of  $p$  symmetry, and
  - ✓ 1 of  $d$  symmetry are used.

The four of  $p$  symmetry differ in the  $\alpha$  values (term  $e^{-\alpha r^2}$ ) and for each of these four, we have all three  $p$  functions ( $p_x$ ,  $p_y$  and  $p_z$ ).

- **Often such a basis set is contracted:** One would take the Gaussians and form a smaller set of “fixed” linear combinations:

$$\tilde{\chi}_{R,k,n,l,m}(\vec{r}) = \sum_i u_{ki} \chi_{R,\alpha_i,n,l,m}(\vec{r}).$$

# Gaussian functions

$$\tilde{\chi}_{R,k,n,l,m}(\vec{r}) = \sum_i u_{ki} \chi_{R,\alpha_i,n,l,m}(\vec{r}).$$

- Here the constants  $u_{ki}$  are fixed and only the coefficients to the contracted functions  $\tilde{\chi}$  are optimized within the Hartree-Fock-Roothaan calculations and  $k$  distinguishes different contracted functions.
- The notation is something like [4,2,1], where the numbers give the number of contracted functions (e.g. a linear combination as shown above of  $s$ ,  $p$  and  $d$  symmetry, respectively).
- Often many different functions with the same  $n$ ,  $l$  and  $m$  but differing in the  $\alpha$  are used. Then the  $\alpha$  are often chosen according to (where  $p$  labels the different  $\alpha$ ):

$$\alpha_p = a \cdot b^p,$$

# Gaussian functions

HF molecule	Primitive set	Contracted set	$E_e$ (a.u.)	$R_e$ (a.u.)	$\mu_e$ (a.u.)
	<i>6s3p/3s</i>	<i>2s1p/1s</i>	-98.572844	1.8055	0.49258
	<i>12s6p/6s</i>	<i>2s1p/1s</i>	-99.501718	1.8028	0.51000
	<i>8s4p/4s</i>	<i>3s2p/2s</i>	-99.887286	1.7410	0.89971
	<i>10s4p/4s</i>	<i>3s2p/2s</i>	-99.983425	1.7386	0.90487
	<i>9s5p/4s</i>	<i>3s2p/3s</i>	-100.018895	1.7467	0.95544
	<i>9s5p/4s</i>	<i>3s2p/2s</i>	-100.020169	1.7475	0.96334
	<i>9s5p/5s</i>	<i>3s2p/3s</i>	-100.020665	1.7376	0.96256
	<i>9s5p/4s</i>	<i>4s3p/2s</i>	-100.022946	1.7390	0.93645
	<i>11s6p/5s</i>	<i>4s2p/3s</i>	-100.026364	1.7422	0.91244
	<i>9s5p/4s2p</i>	<i>3s2p/2s1p</i>	-100.034266	1.7257	0.87851
	<i>10s6p/5s</i>	<i>5s3p/3s</i>	-100.036872	1.7380	0.93757
	<i>10s6p/5s</i>	<i>5s4p/3s</i>	-100.037008	1.7371	0.93656
	<i>9s5p/4s2p</i>	<i>4s3p/2s1p</i>	-100.040470	1.7046	0.83604
	<i>11s6p/5s2p</i>	<i>4s2p/3s1p</i>	-100.044050	1.7168	0.84243
	<i>10s6p/5s2p</i>	<i>5s4p/3s1p</i>	-100.044751	1.7206	0.81251
	<i>9s5p2d/4s2p</i>	<i>3s2p1d/2s1p</i>	-100.049112	1.7053	0.74383
	<i>9s5p2d/4s2p</i>	<i>4s3p1d/2s1p</i>	-100.049799	1.7046	0.74154
	<i>11s6p2d/5s2p</i>	<i>4s2p1d/3s1p</i>	-100.057755	1.7036	0.69515
	<i>10s6p1d/5s2p</i>	<i>5s4p1d/3s1p</i>	-100.059724	1.7073	0.74436
	<i>10s6p2d/5s2p</i>	<i>5s3p1d/3s1p</i>	-100.062343	1.7027	0.74871

[From Springborg](#)

Results of different calculations on an HF molecule with increased size of the basis set. The total energy decreases with increasing basis-set size, as it should according to the variational principle. The optimized bond-length appears to converge, whereas the dipole moment shows a much slower convergence.

# Gaussian functions

HF molecule	Primitive set	Contracted set	$E_e$ (a.u.)	$R_e$ (a.u.)	$\mu_e$ (a.u.)
	6s3p/3s	2s1p/1s	-98.572844	1.8055	0.49258
	12s6p/6s	2s1p/1s	-99.501718	1.8028	0.51000
	8s4p/4s	3s2p/2s	-99.887286	1.7410	0.89971
	10s4p/4s	3s2p/2s	-99.983425	1.7386	0.90487
	9s5p/4s	3s2p/3s	-100.018895	1.7467	0.95544
	9s5p/4s	3s2p/2s	-100.020169	1.7475	0.96334
	9s5p/5s	3s2p/3s	-100.020665	1.7376	0.96256
	9s5p/4s	4s3p/2s	-100.022946	1.7390	0.93645
	11s6p/5s	4s2p/3s	-100.026364	1.7422	0.91244
	9s5p/4s2p	3s2p/2s1p	-100.034266	1.7257	0.87851
	10s6p/5s	5s3p/3s	-100.036872	1.7380	0.93757
	10s6p/5s	5s4p/3s	-100.037008	1.7371	0.93656
	9s5p/4s2p	4s3p/2s1p	-100.040470	1.7046	0.83604
	11s6p/5s2p	4s2p/3s1p	-100.044050	1.7168	0.84243
	10s6p/5s2p	5s4p/3s1p	-100.044751	1.7206	0.81251
	9s5p2d/4s2p	3s2p1d/2s1p	-100.049112	1.7053	0.74383
	9s5p2d/4s2p	4s3p1d/2s1p	-100.049799	1.7046	0.74154
	11s6p2d/5s2p	4s2p1d/3s1p	-100.057755	1.7036	0.69515
	10s6p1d/5s2p	5s4p1d/3s1p	-100.059724	1.7078	0.74436
	10s6p2d/5s2p	5s3p1d/3s1p	-100.062343	1.7027	0.74871

[From Springborg](#)

The notation used here is as follows: A primitive set of the type 6s3p/3s means that 6 Gaussians of s type and three p type on fluorine and 3 of s type on hydrogen have been used. These were subsequently contracted to 2s1p/1s, which means two contracted Gaussians of s type on fluorine, 1 of p type on fluorine, and 1 of s type on hydrogen. The original work is [from Daudel \(1983\)](#)

# Expanding Slater orbitals in Gaussians

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- The variational principle gives accurate total energy but other properties may be far from converged when the total energy seems to be converged.
- One may use Slater-type orbital by expanding those in terms of Gaussians so that the integrals can be evaluated easily. This leads to basis sets like, e.g., STO-3G, which means that each Slater-type orbital is expanded in 3 Gaussians.
- A basis set of the type STO 4-31G is one that could be used for a second-row atom. The notation means that the core 1s electrons are described by expanding the Slater-type orbitals in four Gaussians, whereas the valence 2s and 2p orbitals are expanded in three and one Gaussians, respectively.
- A larger basis set can be obtained by adding polarization functions. For instance, the notation 4-31G\*\* indicates that d functions have been added to the basis set for second- and third-row atoms (the first \*), whereas the second \* shows that p polarization functions have been added to the basis set for hydrogen atoms.
- Access to various Gaussian sets are provided [on this web site by DOE](#). You may also want to consult [the theoretical chemistry tutorials](#).

# Plane waves

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- The Slater-type orbitals are closely related to the true eigenfunctions for single electron ions, and have been devised using chemical intuition.
- Also the Gaussians are well localized to specific atoms.
- A completely different approach is used when using plane waves as basis functions:

$$\chi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}$$

- These are completely delocalized and can therefore not be ascribed individual atoms. They are the correct eigenfunctions for free electrons and as such they can be considered good basis functions for studies on metals.
- They are also used in DFT studies on molecular systems.

# Plane waves

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$$\chi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}$$

- ▶ They have two advantages: At first, it is very easy to calculate all kinds of matrix elements (using fast-Fourier-transform techniques) and second, the size of the basis set can be increased systematically in a very simple way.
- ▶ Their main disadvantages are that the basis sets very easily become very large, and that it is less trivial to interpret the results in terms of chemical bonds.

# Numerical basis functions

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- A few methods use basis functions that are represented completely numerically and obtained for the isolated atoms as well as some relevant ions. Thus, for CO one may construct numerical basis functions by considering the isolated C and O atoms as well as C<sup>+</sup> and O<sup>-</sup> ions. All basis functions are then represented in the form

$$\chi(\vec{r}) = R_{nl}(r)Y_{lm}(\theta, \phi).$$

- Only the radial part  $R_{nl}(r)$  is given numerically. These methods require that all integrals are calculated numerically.

# Augmented waves

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- A compromise between the earlier discussed basis sets is offered by the augmented waves.
- We focus on the potential felt by a valence electron. Close to the nuclei this potential is dominated by that of the nucleus and the core electrons and is therefore largely spherically symmetric.
- Further away from all nuclei the potential varies much more slowly. One may therefore consider a simplified potential

$$V(\vec{r}) = \begin{cases} V_s(|\vec{r} - \vec{R}|) & \text{for } |\vec{r} - \vec{R}| \leq s_{\vec{R}} \\ V_0 & \text{in the interstitial region.} \end{cases}$$

- Here  $V_s(|\vec{r} - \vec{R}|)$  is the spherically symmetric part of the potential around the nucleus at  $\vec{R}$ ,  $s_{\vec{R}}$  is the radius of a sphere where the spherically symmetric part of the potential is used, and  $V_0$  is a constant.

# Augmented waves

$$\left[-\frac{1}{2}\nabla^2 + V(\vec{r})\right] \chi(\vec{r}) = \varepsilon \cdot \chi(\vec{r})$$

- The single-particle Schrödinger equation for this potential can be solved numerically inside the sphere and analytically in the interstitial region. This

leads then to basis functions that are given as either plane waves  $e^{i\vec{k}\cdot\vec{r}}$

or as spherical waves  $h_l^{(1)}(\kappa r)Y_{lm}(\theta, \phi)$  spherical Hankel function  
(centered in the origin) As  $k \rightarrow 0$ ,  $h_l^{(1)}(\kappa r) \rightarrow r^{-l-1}$

in the interstitial region. These functions are then augmented inside the sphere with numerically given functions.

- If the plane waves are used, one arrives at **augmented planewave methods** (APW), and with the spherical waves one arrives at **augmented spherical wave** (ASW) or **muffin-tin-orbital** (LMTO) methods.
- Their advantages are the transparency in interpreting the results and that only small-sized basis sets are necessary for obtaining accurate results.

# Augmented waves

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- ▶ The main disadvantage is the separation of space into spheres and interstitial region, whereby the calculation of matrix elements becomes non-trivial.
- ▶ These basis sets are applied with DFT, where the single-particle equation has a simple meaning, and that the potential is used solely in constructing the basis functions - not solving the Schrödinger equation.

# Symmetry

- Let us return to the Hartree-Fock-Roothaan equations:

$$\sum_{m=1}^{N_b} \left\{ \langle \chi_p | \hat{h}_1 | \chi_m \rangle + \sum_{i=1}^N \sum_{n,q=1}^{N_b} c_{ni} c_{qi}^* [\langle \chi_p \chi_q | \hat{h}_2 | \chi_m \chi_n \rangle - \langle \chi_q \chi_p | \hat{h}_2 | \chi_m \chi_n \rangle] \right\} c_{ml}$$

$$= \varepsilon_l \sum_{m=1}^{N_b} \langle \chi_p | \chi_m \rangle c_{ml}$$

- A number of one-electron  $\langle \chi_p | \hat{h}_1 | \chi_m \rangle$  and  $\langle \chi_p | \chi_m \rangle$ .

and two-electron integrals need to be calculated:  $\langle \chi_p \chi_q | \hat{h}_2 | \chi_m \chi_n \rangle$

where:  $\hat{h}_1(\vec{r}) = -\frac{1}{2} \nabla^2 - \sum_{k=1}^M \frac{Z_k}{|\vec{R}_k - \vec{r}|}$        $\hat{h}_2(\vec{r}_i, \vec{r}_j) = \frac{1}{|\vec{r}_i - \vec{r}_j|}$

# Symmetry adapted basis functions

- In order to reduce the number of the integrals that are non-vanishing it is advantageous to use symmetry-adapted basis functions.
- This means that, from basis functions that are centered at different atoms, (but are equivalent due to symmetry), **we construct linear combinations so that these transform according to given irreducible representations of the group describing the symmetry of the system.**
- This procedure does not work, however, for plane waves (since these are not centered at any site). Since both  $\hat{h}_1$  and  $\hat{h}_2$  transform according to the 'trivial' irreducible representation, we obtain that  $\langle \chi_p | \hat{h}_1 | \chi_m \rangle$  and  $\langle \chi_p | \chi_m \rangle$  can be non zero if  $\chi_p$  and  $\chi_m$  transform to the same irreducible representation.
- The terms  $\langle \chi_p \chi_q | \hat{h}_2 | \chi_m \chi_n \rangle$  can be non-zero, when the direct product of the irreducible representations of  $\chi_p$ , and  $\chi_q$ , and the direct product of the irreducible representations of  $\chi_m$ , and  $\chi_n$ , contain at least one common irreducible representation.

# Symmetry adapted basis functions

- These results are very simple to apply for systems with one-dimensional translational or screw-axis symmetry.
- Here, the continuous variable  $k$  is used in characterizing the irreducible representations, and we find thus that the matrix elements of  $\langle \chi_p | \hat{h}_1 | \chi_m \rangle$  and  $\langle \chi_p | \chi_m \rangle$  can be non-zero only if  $k_m - k_p = 0$  (modulo  $2\pi$ )
- Similarly, those of  $\langle \chi_p \chi_q | \hat{h}_2 | \chi_m \chi_n \rangle$  are non-zero if

$$k_m + k_n - k_p - k_q = 0 \text{ (modulo } 2\pi\text{)}.$$

Here,  $k_r$  is  $k$  for the symmetry-adapted basis function  $\chi_r$ .

# Basis set superposition error

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- Consider a single system and for this a single orbital that is described approximately through a finite set of basis functions

$$\psi_i(\vec{x}) = \sum_{j=1}^{N_b} \chi_j(\vec{x}) c_{ji}$$

- Based on the variational principle, whenever this basis set is extended through further functions, the quality of the calculation is improved and the electronic energy is lowered.
- Let us now add one more system for which we describe the orbitals through a finite basis set.
- The fact that *any* of the orbitals of each of the two systems can be improved when incorporating more basis functions (here e.g. those that are centered on the other system) means that the total energy of the two systems together may be lower than the sum of the total energies of the two systems individually.

# Functional Boys-Bernardi counterpoise method

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- When the two parts are brought together this will mean that the interaction energies may become overestimated. This is the so-called '**basis set superposition error**'.
- One way to improve this is to consider each of the two isolated systems separately with basis sets that are extended with those of the other system but without including the electrons and nuclei of that system.
- This is the counterpoise method (Boys and Bernardi, 1970)