SCF methods, basis sets, and integrals

Lecture III: Basis sets

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Overview of basis functions

We may try to solve the Hartree–Fock or Kohn–Sham equations on a real-space grid in 3D. Accurate numerical Hartree–Fock methods exist for atoms and diatomic molecules.

Alternatively, we may expand the MOs or crystal wavefunctions in a set of basis functions. Examples include:

- Numerical atomic functions
- Finite elements (FEM)
- Wavelets
- Plane and spherical waves
- Slater-type orbitals (STOs)
- Gaussian-type orbitals (GTOs)

Numerical atomic orbitals

- It is possible to use purely numerical atomic functions that are defined on a real-space grid in three dimensions.
- In density-functional theory (DFT), integrals are computed by a numerical quadrature in 3D.
- $\texttt{DMol}^3$ and `SIESTA` are DFT programs that use numerical atomic orbitals.
- The basis sets used by $\texttt{DMol}^3$ are denoted Minimal, DN, DND, DNP, TNP. Also `SIESTA` uses multiple-zeta and polarisation functions.
- In these programs, DFT is easily implemented in the local-density (LDA) and generalised-gradient approximations (GGA). Hybrid functionals with Hartree–Fock exchange are more difficult.
- The potentials $V_{\mathrm{ne}}(\mathbf{r})$, $J(\mathbf{r})$ and $v_{\mathrm{xc}}(\mathbf{r})$ are local.

Numerical atomic orbitals

- In DFT, without exact exchange, all potentials are local, and the Coulomb potential at a grid point $\mathbf{r}_p$ can be computed as

$$J(\mathbf{r}_p) \approx \sum_{q=1}^{n_{\mathrm{grid}}} w_q \sum_{i=1}^{n_{\mathrm{occ}}} \frac{\varphi_i^*(\mathbf{r}_q)\varphi_i(\mathbf{r}_q)}{|\mathbf{r}_p - \mathbf{r}_q|} = \sum_{q=1}^{n_{\mathrm{grid}}} w_q \frac{\rho(\mathbf{r}_q)}{|\mathbf{r}_p - \mathbf{r}_q|}$$

- The w_q are the appropriate weights of the quadrature.
- Matrix elements of the Coulomb and local exchange–correlation potentials can be computed as

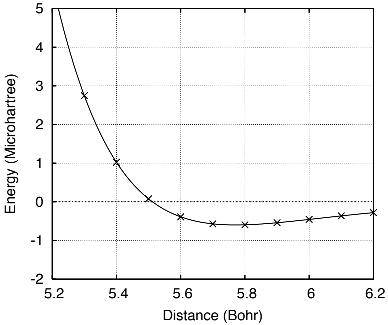
$$\begin{aligned}
\langle \chi_\mu | \hat{J} | \chi_\nu \rangle &= \int \chi_\mu^*(\mathbf{r}) J(\mathbf{r}) \chi_\nu(\mathbf{r}) d\mathbf{r} \approx \sum_{p=1}^{n_{\mathrm{grid}}} w_p \chi_\mu^*(\mathbf{r}_p) J(\mathbf{r}_p) \chi_\nu(\mathbf{r}_p) \\
\langle \chi_\mu | v_{\mathrm{xc}} | \chi_\nu \rangle &= \int \chi_\mu^*(\mathbf{r}) v_{\mathrm{xc}}(\mathbf{r}) \chi_\nu(\mathbf{r}) d\mathbf{r} \approx \sum_{p=1}^{n_{\mathrm{grid}}} w_p \chi_\mu^*(\mathbf{r}_p) v_{\mathrm{xc}}(\mathbf{r}_p) \chi_\nu(\mathbf{r}_p)
\end{aligned}$$

Numerical molecular orbitals

- Some DFT implementations (such as Octopus) attempt to describe the molecular Kohn–Sham orbitals on a real-space grid.
- A 3D simulation box is chosen together with a grid spacing, for example 0.5 a_0. Then, a grid in 3D is constructed and the SCF equations are solved on the grid.
- This is different from an MO-LCAO expansion in numerical AOs!
- Pseudopotentials are inevitable for real-space grid methods, but they are not required when numerical AOs are used.
- A great advantage of the use of numerical AOs as in $\mathtt{DMol}^3$ is that the method is free of the basis-set superposition error (BSSE).
- Because exact atomic orbitals are used, the atoms in a molecule cannot improve their orbitals artificially using basis functions from other atoms.

Basis-set superposition error (BSSE)

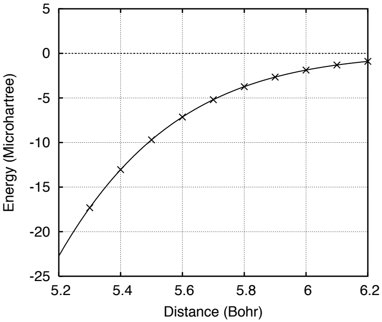
- A famous example of BSSE is the Hartree–Fock calculation of the He$\cdots$He potential curve in a two-function 3-21G basis:



- The RHF/3-21G calculation of He$\cdots$He yields an interaction energy of $-0.6\ \mu E_\mathrm{h}$ at $R = 5.77\ a_0$.
- The Hartree–Fock curve should be purely repulsive!
- Accidentally, the Hartree–Fock minimum is close to the true minimum at $5.60\ a_0$. The true well depth amounts to ca. $-35\ \mu E_\mathrm{h}$.
- The RHF/3-21G energy of the He atom is in error by $26\ \mathrm{m}E_\mathrm{h}$.

Basis-set superposition error (BSSE)

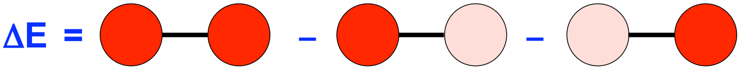
- Let us compute the RHF/3-21G energy of one He atom while another 3-21G basis (without atom) is approaching.



- Shown is the computed energy relative to the RHF calculation in only the atom's own 3-21G basis.
- This is the BSSE: artificial energy lowering due to neighbouring functions.
- At $R = 5.77\ a_0$, the artificial energy lowering is $-4.1\ \mu E_\mathrm{h}$/atom ($-8.2\ \mu E_\mathrm{h}$ for both atoms).
- We should add $8.2\ \mu E_\mathrm{h}$ to the computed interaction energy of $-0.6\ \mu E_\mathrm{h}$.

The counterpoise correction

- Thus, at $R = 5.77\ a_0$, we obtain a repulsive potential of $+7.6\ \mu E_{\mathrm{h}}$ at the RHF/3-21G level if we correct for BSSE.
- This correction is known as counterpoise correction. It consists of computing not only the system of interest but also its fragments in the basis set of the whole system.
- The interaction energy is computed by subtracting the energies of the fragments computed in the whole basis.



- In practice, the basis set in a counterpoise calculation is most easily defined by setting the nuclear charge of the corresponding atom to zero (ghost atom).

The counterpoise correction

- The CP-corrected interaction energy is directly obtained by calculating both the system and the fragments in the same basis,

$$\Delta E_{\text{CP corrected}} = E_{\text{AB}} - E_{\text{A+ghost(B)}} - E_{\text{B+ghost(A)}}$$

- The CP corrections to fragments A and B are defined as follows:

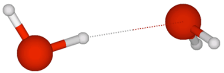
$$\delta_{\text{CP}}(\text{A}) = E_{\text{A}} - E_{\text{A+ghost(B)}}, \qquad \delta_{\text{CP}}(\text{B}) = E_{\text{B}} - E_{\text{B+ghost(A)}}$$

- Hence, the CP-corrected interaction energy can also be computed from

$$\Delta E_{\text{CP corrected}} = \Delta E_{\text{CP uncorrected}} + \delta_{\text{CP}}(\text{A}) + \delta_{\text{CP}}(\text{B})$$
$$\Delta E_{\text{CP uncorrected}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}}$$

- Using numerical AOs, $E_{\text{A}} = E_{\text{A+ghost(B)}} = E_{\text{A}}(\text{exact})$!

Counterpoise corrected binding energies



- Usually, free fragments have another geometry than in the complex (such as the H_2O dimer).

- The binding energy is the energy of the complex or supermolecule in its optimized geometry relative to the energies of the dissocation products in their own, optimized geometries,

$$E_{\text{binding energy}} = \Delta E^{(1)} + \Delta E^{(2)} = \Delta E_{\text{CP corrected}} + \Delta E^{(1)}$$

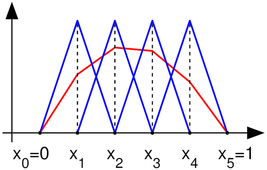
- $\Delta E^{(1)}$ is a one-body term. It contains the relaxation energy of the dissociation products,

$$\Delta E^{(1)} = E_{\text{A, complex geom.}} - E_{\text{A, relaxed geom.}} + \text{same for B}$$

- As defined here, the binding energy is a negative quantity. Often, however, it is reported as a positive value.

Finite elements methods (FEM)

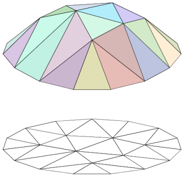
- The finite-element method is an expansion method which uses a strictly local, piecewise polynomial basis.



$$f(x) = \sum_{k=1}^{4} c_k\, f_k(x)$$

- It combines the advantages of basis-set and real-space grid approaches.
- A finite element is a basis function, which takes the value 1 at a grid point in real space, but which is 0 at its neighbouring grid points and at all other grid points.
- In its simplest form, the basis function is linear between two grid points x_k and x_{k+1}.

Finite elements methods (FEM)



- In 2D, the space is divided up in triangles and the surface is approximated by piecewise linear functions (see figure).
- FEM is also applicable in 3D.

- FEM has been used for benchmark Hartree–Fock and MP2 (2^{nd}-order Møller–Plesset perturbation theory) calculations of atoms (*e.g.*, with partial waves up to $L = 12$).
- FEM has also been used for benchmark calculations of one-electron diatomics and for benchmark DFT calculations of diatomic systems.
- Modern techniques: Hermite interpolation functions, adaptive curvilinear coordinates, separable norm-conserving pseudopotentials, periodic boundary conditions, multigrid methods.

Wavelets

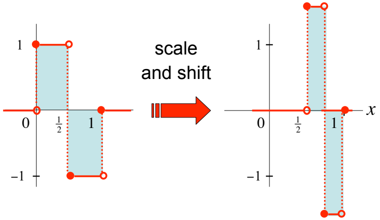
- Wavelets are a relatively new basis set in electronic structure calculations.
- Being localised both in real and in Fourier space, wavelets combine the advantages of local basis-set and plane waves.
- Localised orbitals and density matrices can be represented in a very compact way, and wavelets therefore seem an ideal basis set for $\mathcal{O}(N)$ schemes.
- There exist fast wavelet transforms (FWT).
- As an example, we shall consider the Haar wavelets, but there are many others (*e.g.*, Daubechies wavelets, which can be used in electronic-structure theory).
- The Haar transform is very useful in image compression (JPEG).
- To the author's knowledge, an efficient general-purpose DFT program is not yet available.

Wavelets

- A simple example is the Haar wavelet,

$$h_{mn}(x) = 2^{-m/2} h(2^{-m}x - n) \quad \text{with} \quad h(x) = \begin{cases} 1, & \text{if } 0 \leq x < 1/2 \\ -1, & \text{if } 1/2 \leq x < 1 \\ 0, & \text{otherwise} \end{cases}$$

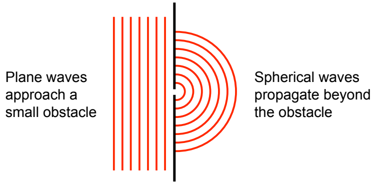
- $h(x)$ is denoted as mother wavelet.
- The wavelets $\{h_{mn}(x)\}$ form an orthonormal basis.



$h_{00}(x) = h(x)$ $\qquad$ $h_{-1,1}(x) = \sqrt{2}\, h(2x - 1)$

Plane (and spherical) waves

- Plane (and spherical) waves are used in DFT codes that treat the electronic structure of condensed matter.
- CPMD, FLEUR, VASP and Wien2K are programs using plane waves.
- The basis functions can be written as



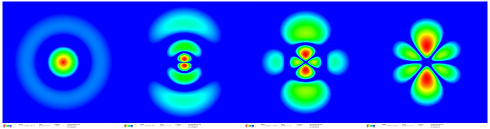
$$U_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \text{ (plane wave)}, \qquad \text{and } U_k(\mathbf{r}) = \frac{e^{ikr}}{r} \text{ (spherical wave)}$$

- Advantage of plane wave codes: After defining a 3D box, the number of plane waves and the basis-set quality is controlled by a single energy-cutoff value. Basis functions up to that energy level are considered.

Pseudopotentials (PPs)

- Disadvantage of plane wave approaches: It is very difficult for plane waves to describe the electronic structure near the nuclei.
- One solution to this problem consists of using (ultra-soft) pseudopotentials (US-PP).
- The idea is that with PPs, the (remaining) eigenstates and the electron density are much smoother than without. Plane waves can only handle a smooth potential well.
- Typical cutoff values range from 10–20 E_{h} for Vanderbilt ultra-soft pseudopotentials, 30–50 E_{h} for Troullier–Martins norm-conserving pseudopotentials to 40–100 E_{h} for Goedecker pseudopotentials (*i.e.*, higher values for less soft PPs).
- With PPs, the number of plane waves is of the order of 100 per atom. Modern programs can treat thousands of valence electrons.

Hydrogen atom eigenfunctions



- The hydrogenic functions seem to form a natural basis for the MO-LCAO Ansatz.
- These are the true atomic functions of hydrogen and H-like ions. The *bounded eigenfunctions* may be written as

$$\psi_{nlm} = R_{nl}(r)\, Y_l^m(\vartheta, \varphi)$$

$$R_{nl}(r) = \left(\frac{2Z}{n}\right)^{3/2} \sqrt{\frac{(n-l-1)!}{2n(n+l)!}} \left(\frac{2Zr}{n}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{n}\right) \exp\left(-\frac{Zr}{n}\right)$$

- The radial part contains an associated Laguerre polynomial L_{n-l-1}^{2l+1} in $2Zr/n$ and an exponential in $-Zr/n$.

Hydrogen atom eigenfunctions

- The H-atom eigenfunctions are the exact solutions for a one-electron Coulombic system, but the functions ψ_{nlm} are not useful as basis functions for many-electron atoms or molecules.
- In 1928, it was already recognised by Born and Hylleraas that the He atom could not be described by a CI expansion using the H-like *bound-state eigenfunctions*.
- To constitute a complete set, the bound-state eigenfunctions must be supplemented by the unbounded continuum states.
- Furthermore, the H-like functions spread out rapidly and become quickly too diffuse for calculations of the core and valence regions of a many-electron atom.

$$\langle \psi_{nlm} | r | \psi_{nlm} \rangle = \frac{3n^2 - l(l+1)}{2Z}$$

- They may be useful to describe Rydberg states.

Hydrogen atom eigenfunctions

- The problem with the H-atom eigenfunctions is that the exponent Z/n in the exponential decreases when n increases,

$$\psi_{nlm} \propto (r/n)^l L_{n-l-1}^{2l+1}(2Zr/n)\exp(-Zr/n)$$

- It seems a good idea to change to functions of the type

$$\chi_{nlm} \propto (\zeta r)^l L_{n-l-1}^{2l+2}(2\zeta r)\exp(-\zeta r)$$

- These Laguerre functions form a complete, orthonormal set in $L^2(\mathbb{R}^3)$.
- Laguerre functions are very useful for highly accurate work on atoms.

Nodeless Slater-type orbitals (STOs)

- We can expand the Hartree–Fock orbital of He in a basis of Laguerre functions,

$$\varphi_{\mathrm{He}}(\mathbf{r}) = \sum_{n=1}^{n_{\max}} c_n L_{n-1}^2(2\zeta r)\exp(-\zeta r)$$

- There is one nonlinear parameter (ζ, which could be determined via $\langle\hat{V}\rangle = -2\langle\hat{T}\rangle$) and we must choose the expansion length.
- Can we fix n and use variable exponents?

$$\varphi_{\mathrm{He}}(\mathbf{r}) = \sum_{k=1}^{k_{\max}} c_k \exp(-\zeta_k r)$$

- Can we even take variable exponents *and* variable powers in r?

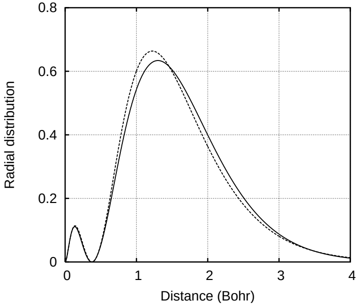
$$\varphi_{\mathrm{He}}(\mathbf{r}) = \sum_{n=1}^{n_{\max}} \sum_{k=1}^{k_{\max}(n)} c_{nk}\, r^{n-1} \exp(-\zeta_{nk} r)$$

Slater-type orbitals (STOs)

The figure shows the radial distribution

$$4\pi r^2 \left[\Phi_{2s}(r)\right]^2$$

of the C atom from a minimal $2s1p$ basis (solid line) and from an extended $6s4p$ basis (dashed line).



In the minimal basis:

$$\varphi_{2s}(r) = -0.231\, N_{1s} \exp(-5.58\, r) + 1.024\, N_{2s}\, r\, \exp(-1.46\, r)$$

In the extended basis:

$$\varphi_{2s}(r) = \sum_{k=1,2} c_{k1} N_{1s} \exp(-\zeta_{k1} r) + \sum_{k=1,4} c_{k2} N_{2s}\, r\, \exp(-\zeta_{k2} r)$$

Slater-type orbitals (STOs)

- Clementi–Roothaan–Yoshimine $6s4p$ STO basis for carbon:

			Coefficients	
STO type	Exponents	$1s$	$2s$	$2p$
$1s$ STO	9.2683	0.07657	−0.01196	
	5.4125	0.92604	−0.21041	
$2s$ STO	4.2595	0.00210	−0.13209	
	2.5897	0.00638	0.34624	
	1.5020	0.00167	0.74108	
	1.0311	−0.00073	0.06495	
$2p$ STO	6.3438			0.01090
	2.5873			0.23563
	1.4209			0.57774
	0.9554			0.24756

$$\varphi_{2s}(r) = -0.01196\, N_{1s}\, \exp(-9.2683\, r) + \cdots + 0.06495\, N_{2s}\, r \exp(-1.0311\, r)$$

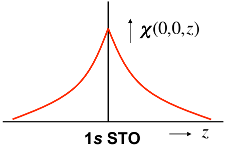
- The extended basis contains $2 + 4 + 4 \times 3 = 18$ basis functions.
- The (Hartree–Fock) coefficients are given with respect to normalised basis functions.
- The linear combinations with the Hartree–Fock coefficients can be used as a minimal basis comprising $1 + 1 + 1 \times 3 = 5$ basis functions (contractions).

Slater-type orbitals (STOs)

Advantages of STOs:

- Correct description of the cusp at the nucleus. For a one-electron system, for example, we have

$$\varphi_{1s} \propto Rr, \qquad \left.\frac{\partial R(r)}{\partial r}\right|_{r=0} = -Z\,R(0) \neq 0$$



- STOs have the correct asymptotic long-range behaviour,

$$\varphi_{\mathrm{HOMO}} \propto \exp(-\zeta r), \quad \zeta = \sqrt{2 \cdot \mathrm{IP}} = \sqrt{2 \cdot |\varepsilon_{\mathrm{HOMO}}|}$$

- Accurate calculations are possible for atoms and diatomics.

Slater-type orbitals (STOs)

Disadvantages of STOs:

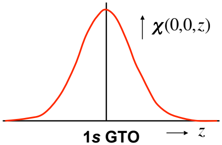
- No efficient program available to evaluate the many-centre two-electron STO integrals.
- Long-range behaviour of the density is correct only if the smallest STO exponent is $\zeta_{\min} = \sqrt{2 \cdot \text{IP}}$. Stable molecules have IP > 5 eV. Hence, ζ should not be smaller than $0.6\ a_0^{-1}$, but lower values are often required for accurate work on molecules.

A program that uses STOs is ADF.

- The basis sets used by this program are denoted SZ, DZ, DZP, TZP, TZ2P.

Gaussian-type orbitals (GTOs)

- In molecular calculations, the many-centre integrals are much easier to compute with Gaussian-type orbitals,



$$\chi(\mathbf{r}) \propto x^k y^l z^m \exp(-\alpha r^2)$$

  - GTOs have no cusp at the nucleus, but this is not a main concern in chemical applications.
  - The cusp occurs with point charges. For more realistic nuclei with finite extension, the Gaussian shape is actually more realistic.
  - GTOs have the wrong asymptotic long-range behaviour, but the error due to falling off too quickly is less severe than the too long tail of an STO with too small exponent.
  - Accurate calculations are possible for polyatomic molecules!
  - In terms of accuracy/effort, GTOs win over STOs.

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Gaussian basis sets: Overview

- Minimal basis sets (STO-nG)
- Double-zeta basis sets (DZ, SV, 6-31G)
- Pople basis sets (6-311G*, 6-311+G(2df,2pd), etc.)
- Karlsruhe “def2” basis sets
- Polarisation-consistent basis sets (pc-n)
- Atomic natural orbital (ANO) basis sets
- Correlation-consistent basis sets (cc-pVXZ)
- Special-purpose basis sets (IGLO, Sadlej)
- Effective core potentials (*e.g.*, LANL2DZ)
- Auxiliary basis sets (RI-J, RI-JK, “cbas”, “cabs”)

Gaussian basis sets: Purpose

- Choosing the right basis depends much on the type of calculation that we want to perform.
- Be aware that different basis sets are needed for Hartree–Fock and DFT calculations on the one hand and electron-correlation calculations (MPn, CI, CC) on the other.
- The electron density of negative ions may be extended in space and GTOs with small exponents are required (diffuse functions).
- For some properties, the region near the nucleus is important (*e.g.*, electric field gradient at the nucleus, Fermi contact term). Then, GTOs with large exponents are required (tight functions).
- Van der Waals intermolecular interactions need diffuse functions and are different from strongly covalently bound molecules.
- Be aware of the BSSE.

STO-nG basis sets

- The STO-nG basis sets are minimal basis sets.
- The idea is to represent a Slater-type orbital (STO) by a linear combination of GTOs.
- In the STO-3G basis, for example,

$$N\ \exp(-\zeta\, r) \approx \sum_{k=1}^{3} c_k\, N_k\ \exp(-\alpha_k\, r^2)$$

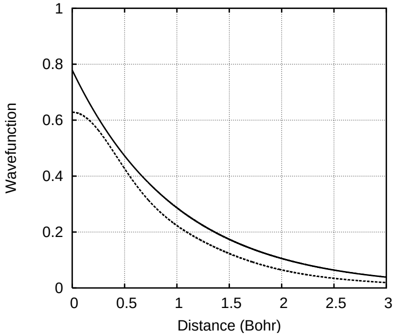
- For hydrogen, the following STO-3G basis represents the standard STO with exponent $\zeta = 1.24\ a_0^{-1}$:

k	1	2	3
α_k/a_0^{-2}	3.42525091	0.62391373	0.1688554
c_k	0.15432897	0.53532814	0.4446345

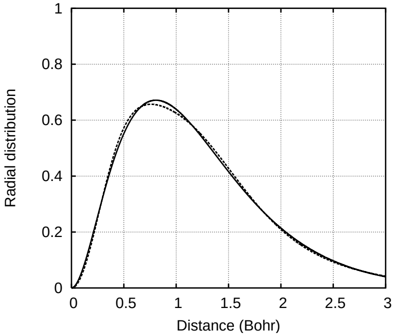
- The exponents α_k and contraction coefficients c_k are obtained by a least-squares fit. A contraction is one single basis function, which itself is a fixed linear combination of (primitive) GTOs.

STO-nG basis sets

The H-atom STO-3G function (dashed line) replaces an STO with $\zeta = 1.24$ (solid line).



$\chi(r)$

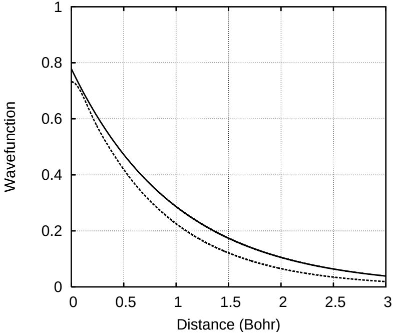


$4\pi\, r^2\, \chi^2(r)$

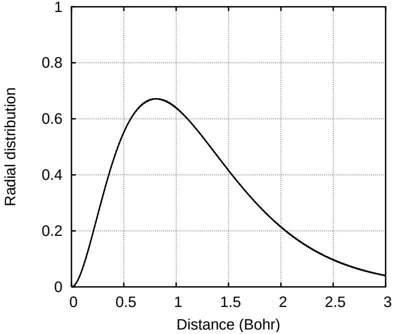
The figure on the left shows that the STO-3G basis function has no cusp at $r = 0$.

STO-nG basis sets

The H-atom STO-6G function (dashed line) replaces an STO with $\zeta = 1.24$ (solid line).



$\chi(r)$



$4\pi\, r^2\, \chi^2(r)$

The figure on the left shows that the STO-6G basis function has no cusp at $r = 0$.

STO-nG basis sets

- STO-3G basis sets exist for the atoms H–I.
- STO-6G basis sets exist for all atoms H–Kr.
- The exponents of the primitive Gaussians are chosen in a special manner. The same exponents are chosen for the various angular momenta in an atomic shell.
- For example, the same three exponents 7.295991196, 2.841021154 and 1.250624506 are used to replace the $4s$, $4p$ and $4d$ STOs of iodine by Gaussians.
- Choosing the same exponents may speed up the integral evaluation significantly, but not all programs exploit this opportunity.
- If a certain STO-nG basis function substitutes an STO with exponent ζ, then a similar STO-nG basis function with exponents $\alpha'_k = \alpha_k \times (\zeta'/\zeta)^2$ replaces an STO with exponent ζ'.

Cartesian versus spherical-harmonic GTOs

- We may want to use Cartesian GTOs—centred at the centre $\mathbf{A}$ (usually an atom)—of the form

$$\chi(\mathbf{r};\alpha,k,l,m,\mathbf{A}) = N_{klm,\alpha}(x-x_A)^k(y-y_A)^l(z-z_A)^m\exp(-\alpha|\mathbf{r}-\mathbf{A}|^2)$$

- A set of f-type functions ($l=3$) is then defined by all combinations with $k+l+m=3$. This yields 10 Cartesian f-type functions. Similarly, there are 6 Cartesian d-type functions, etc.
- The linear combination of 3 of the 6 Cartesian d-type functions corresponds to an $3s$-type function ($x^2+y^2+z^2$). Similarly, the 10-component f-set contains three $4p$-type functions: $(x^2+y^2+z^2)x$, etc.
- It is much better to use the spherical-harmonic GTOs ($5d$, $7f$, $9g$, etc.) in the place of Cartesian GTOs to avoid near-degeneracies in the basis set. Most programs do this, but note that some standard basis-set definitions imply that they are Cartesian.

Double-zeta and split-valence basis sets

- The double-zeta (DZ) basis set consists of two basis functions per atomic orbital and is twice as large as the minimal basis set.
- The split-valence (SV) basis is a minimal basis for core orbitals and is of double-zeta quality for the valence shell.
- Examples of SV basis sets are the 3-21G (atoms H–Cs), 4-31G (atoms H–Ne, P–Cl) and 6-31G (H–Zn) basis sets.
- The notation "6-31G" means that 6 primitive GTOs are contracted to one basis function to describe the core orbitals. Furthermore, 3 primitive GTOs are contracted to the first basis function for the valence shell while another GTO is used as second basis function.
- Also in (most of) these basis sets, the exponents are constraint to be equal in ns and np shells.

Polarisation functions

- The inclusion of a set of polarisation functions is often indicated by “P” or by an asterisk.
- Polarisation functions are basis functions with angular momentum that is not occupied in the atom, for example, p-type functions of H or d-type functions on O.
- Polarisation functions are important when polarisation is important.
- For example, the dipole moment of H_2O amounts to $0.96\ ea_0$ in the SV basis but to $0.83\ ea_0$ in the SVP basis.
- Another example is the barrier to rotation in H_2O_2. The interaction between the dipoles along the polar OH bonds must be described accurately with polarisation functions.
- The polarisation functions are not always added to the H atoms. They *are* in sets denoted as 6-31G** and SVP but *not* in sets denoted 6-31G* and SV(P).

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Valence triple-zeta plus polarisation

- Recommended for molecular SCF calculations: basis sets such as SV(P), SVP, 6-31G* or 6-31G**.
- For accurate SCF calculations, triple-zeta basis sets may be used. They are usually used with polarisation functions,
  - 6-311G*: three contractions (311) for the valence shell, no polarisation functions on H.
  - 6-311G**: same as 6-311G* but with pol. func. on H.
  - 6-311G(2df,2pd): same as 6-311G* but with $2p1d$ polarisation set on H and $2d1f$ set on other atoms.
  - 6-311G(3df,3pd): same as 6-311G(2df,2pd) but with 3 d and 3 p sets.
  - def2-TZVP: valence triple-zeta plus $1p$ polarisation for H, $2d1f$ for B–Ne and Al–Ar, $1p1d1f$ for Sc–Zn.
  - def2-TZVPP: similar to def2-TZVP but with $2p1d$ polarisation for H.

Recommendations for Hartree–Fock and DFT

- For routine work: SV(P) or 4-31G* or pc-1.
- For accurate work: def2-TZVP or 6-311G* or pc-2.
- For very accurate work: def2-TZVPP or 6-311G** or 6-311G(2df,2pd) or pc-3.

For some applications, diffuse functions must be added to obtain accurate (or even meaningful) results.

- A plus sign is added to the basis (6-311+G*, 6-311+G(2df,2pd), etc.) when diffuse functions are added to the nonhydrogen atoms.
- Two plus signs are added when also the H atoms carry diffuse functions (6-311++G**, 6-311++G(2df,2pd), etc.)
- Diffuse functions are for instance required for anions, polar bonds, weak intermolecular interactions, Rydberg orbitals and excitation energies.

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“def2” sets from the `Turbomole` basis-set library

- The “def2” basis sets form a system of segmented contracted basis sets for the elements H–Rn for different levels of flexibility/accuracy.
- The basis sets are denoted def2-SV(P) to def2-QZVPP. They are designed to give similar errors all accross the periodic table for a given basis-set type.
- At the Hartree–Fock and DFT levels, the extended QZVPP basis yields atomisation energies (per atom) with an error < 1 kJ/mol with respect to the basis-set limit. Other sets yield (in kJ/mol):

Basis	Hartree–Fock		DFT (BP-86)	
	mean	σ	mean	σ
def2-SV(P)	-14.5	15.3	-5.8	9.8
def2-SVP	-8.9	10.4	-2.0	8.8
def2-TZVP	-3.7	3.4	-2.6	2.1
def2-TZVPP	-2.0	2.2	-1.1	1.7
def2-QZVP	-0.2	0.6	-0.1	0.4

Polarisation-consistent basis sets (pc-n)

- Higher angular momentum functions are included based on energetical importance in Hartree–Fock calculations.

Atom	pc-0	pc-1	pc-2	pc-3	pc-4
C	$3s2p$	$3s2p1d$	$4s3p2d1f$	$6s5p4d2f1g$	$8s7p6d3f2g1h$
Si	$4s3p$	$4s3p1d$	$5s4p2d1f$	$6s5p4d2f1g$	$7s6p6d3f2g1h$

- Systematic basis sets (pc-n with $n = 0, 1, 2, 3, 4$) for which results converge monotonically to the Hartree–Fock limit. The Hartree–Fock energy obtained in a basis with angular momentum functions up to L is well described by

$$E_L = E_\infty + A(L+1)\exp(-B\sqrt{L})$$

- The pc-n basis sets are available for the elements H–Ar and can be augmented with diffuse functions (aug-pc-n).
- These basis sets use a general contraction scheme.

Segmented versus general contractions

- Consider the pc-1 basis for carbon ($3s2p1d$), which is of “double-zeta plus polarisation (DZP)” quality.

```
S-TYPE FUNCTIONS
    7    3
1252.600000000   0.005573400   0.000000000   0.000000000
 188.570000000   0.041492000   0.000277450   0.000000000
  42.839000000   0.182630000   0.002560200   0.000000000
  11.818000000   0.461180000   0.033485000   0.000000000
   3.556700000   0.449400000   0.087579000   0.000000000
   0.542580000   0.000000000  -0.537390000   0.000000000
   0.160580000   0.000000000   0.000000000   1.000000000
P-TYPE FUNCTIONS
    4    2
   9.142600000   0.044464000   0.000000000
   1.929800000   0.228860000   0.000000000
   0.525220000   0.512230000   0.000000000
   0.136080000   0.000000000   1.000000000
D-TYPE FUNCTIONS
    1    1
   0.800000000   1.000000000
```

- The input for a program that cannot handle general contractions must list an s-type CGTO built from the first 5 primitive GTOs, a second s-type CGTO built from the primitives 2–6, etc.

Performance of various basis sets (test set)

- The table shows mean absolute deviations in r_e (pm), ω_e (cm^{-1}) and intensity (km/mol) relative to the Hartree–Fock limit.

Basis	Size	$\delta(r_e)$	$\delta(\omega_e)$	δ(Intensity)
STO-3G	9	5.5	142.3	22.8
pc-0	13	8.2	60.9	19.0
SVP	18	1.6	14.1	5.2
6-31G*	18	1.5	11.9	7.6
pc-1	18	1.8	11.8	5.4
cc-pVTZ	34	0.7	4.9	2.3
pc-2	34	0.3	3.1	4.3
cc-pVQZ	59	0.3	2.5	1.2
pc-3	64	< 0.1	0.3	0.9

Performance of various basis sets for S_2

The table shows deviations in D_e (kJ/mol), r_e (pm) and ω_e (cm^{-1}) relative to the ROHF Hartree–Fock limit.

Basis	Size	$\delta(D_e)$	$\delta(r_e)$	$\delta(\omega_e)$
pc-0	13	-220	20.3	-148
pc-1	18	-60	2.1	-17
pc-2	34	-19	0.5	-6
pc-3	64	-1	< 0.1	< 1
SV	13	-235	17.1	-178
def2-SVP	18	-47	1.7	-3
def2-TZVP	37	-7	0.2	-2
def2-TZVPP	42	-6	0.2	-2
def2-QZVP	70	-2	< 0.1	< 1

- No significant difference between basis sets of similar size.

Relevance of basis-set errors

The table shows the Hartree–Fock value and various further contributions to the harmonic vibrational frequency of N_2.

Contribution	ω_e / cm^{-1}
Near Hartree–Fock limit	$2\,730.5$
fc-CCSD(T) contribution (near basis-set limit)	-367.1
fc-CCSDTQ contribution (cc-pVTZ basis)	-9.1
fc-CCSDTQ5 contribution (cc-pVDZ basis)	-3.9
Core-correlation contribution	9.8
Relativistic correction (Dirac-Coulomb)	-0.8
Breit correction	-0.5
Calculated value	$2\,358.9$
Experimental value	$2\,358.6$

- Hartree–Fock theory tends to overestimate vibrational frequencies (by ca. 10%). Basis-set errors of the order of 1% are therefore fully acceptable.

Concluding remarks on CGTO basis sets for SCF

- It is recommended to run applications in a “double-zeta plus polarisation”-type basis (DZP). For example,
  - def2-SV(P): for H–Rn and programs that work efficiently with segmented contractions.
  - pc-1: for H–Ar and programs that work efficiently with general contractions.
- It is recommended to investigate basis-set effects by repeating the DZP calculation in a "triple-zeta plus polarisation”-type basis. For example,
  - def2-TZVP: for H–Rn and segmented contractions.
  - pc-2: for H–Ar and general contractions.
- Similar procedures apply to STOs (DZP and TZP in `ADF` and numerical AOs (DNP and TNP in `DMol`^{3}).
- Need for diffuse functions must be checked.

Atomic natural orbital (ANO) basis sets

- ANO basis sets are available for the atoms H–Cm.
- These are large generally contracted basis sets that are particularly useful in electron-correlation (also denoted post-Hartree–Fock) calculations.
- The contraction coefficients are the natural orbitals obtained from atomic post-Hartree–Fock calculations (*e.g.*, CISD, MCPF).
- Various states (also of ions) are averaged. Examples are:

	Primitives	CGTOs	Hartree–Fock range
H	$8s4p3d$	$6s4p3d$	$2s1p - 3s2p1d$
O	$14s9p4d3f$	$7s7p4d3f$	$3s2p1d - 4s3p2d1f$
S	$17s12p5d4f$	$7s7p5d4f$	$4s3p2d - 5s4p3d2f$
Zn	$21s15p10d6f4g$	$8s7p6d5f4g$	$5s3p2d - 6s5p4d3f2g$

- Can be systematically enlarged and BSSE is small.

Correlation-consistent basis sets

- Analogous to ANOs, the aim of the correlation-consistent basis sets is to form systematic sequencies of basis sets of increasing size and accuracy.
- Usually, the correlation-consistent basis sets have generally contracted inner shells.
- They are particularly useful in electron-correlation calculations.
- Polarisation functions are added in groups that contribute almost equally to the correlation energy.
- In their simplest form, they are denoted cc-pVXZ, with X = D, T, Q, 5 ,6). “D” for “double-zeta”, “T” for “triple-zeta”, and so on.
- Diffuse functions can be added (aug-cc-pVXZ) as well as function to correlate the inner shells (aug-cc-pCVXZ, aug-cc-pwCVXZ).
- Basis sets such as aug-cc-pV(X+d)Z, cc-pVXZ-PP and cc-pVXZ-F12 exist for selected atoms.

MP2 correlation energies

- Valence-shell MP2 correlation energies of benzene. The basis-set limit is estimated as $\Delta E_{\mathrm{MP2}} = -1.0575 \pm 0.0005\ E_{\mathrm{h}}$.

Basis	Size	ΔE_{MP2}/%	$\Delta E_{\mathrm{MP2\text{-}F12}}$/%
aug-cc-pVDZ	192	76.8	98.4
aug-cc-pVTZ	414	91.2	99.6
aug-cc-pVQZ	756	96.1	99.9
aug-cc-pV5Z	1242	97.9	100.0
aug-cc-pV6Z	1896	98.8	
def2-TZVP	222	88.2	99.1
def2-TZVPP	270	89.7	99.3
def2-QZVP	522	95.3	99.8

- Slater-type geminals of the form $c_{ij}^{kl}\,\varphi_k(\mu)\varphi_l(\nu)\ \exp(-1.5\,r_{\mu\nu})$ were used in the MP2-F12 method for each orbital pair ij.
- With standard MP2, extremely large basis sets are required to capture 98%.

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Special-purpose basis sets / ECPs

- Most basis sets have been optimised with respect to the total energy of an atom (or molecule).
- There exist basis sets that have been developed for the calculations of optical, electric or magnetic properties.
- Examples are the Sadlej basis sets for electric properties (dipole moment, polarisability) or the IGLO basis sets for NMR chemical shifts.
- In general, calculations of electric properties require diffuse functions. When those are added to all angular-momentum shells of a given basis, the prefix aug is added to the basis (aug-cc-pVXZ, aug-pc-n).
- Sometimes, still more diffuse sets are required (d-aug- and t-aug- sets for polarisabilites and hyperpolarisabilities).
- Tight functions must be added when the wavefunction close to a nucleus is important (*e.g.*, electric-field gradient).

Auxiliary basis sets

- Thus far, we have discussed basis sets for the expansion of MOs and the electronic wavefunction.
- It is possible to save lots of computer time in DFT calculations when the electron density is expanded in a basis set,

$$\rho(\mathbf{r}) \approx \sum_P c_P^\rho \chi_P(\mathbf{r})$$

- In `Turbomole` nomenclature, such a basis is denoted jbas auxiliary basis.
- When also orbital products $\varphi_i \chi_\kappa$ are expanded to build the exchange matrix, a jkbas auxiliary basis is needed.
- For the products $\varphi_i \varphi_a$ that occur in MP2/CC2 theory, a cbas auxiliary basis is used.
- Again other auxiliary basis sets are used in explicitly-correlated methods (cabs).

Closing remarks on basis sets

- For Hartree–Fock (and DFT), the ANO and correlation-consistent basis sets have no advantages over SVP/pc-1 respectively TZVPP/pc-2.
- Basis sets of at least quadruple-zeta quality are required for electron-correlation treatments.
- For very accurate electron-correlation calculations, basis sets larger than cc-pVQZ etc. are needed, in conjunction with basis-set extrapolation.
- Experience with explicitly-correlated theory using Slater-type geminals (two-particle basis functions) indicates that basis sets beyond triple-zeta quality are no longer needed.
- Recipes:
  - def2-SV(P) for DFT, check results with def2-TZVP.
  - def2-TZVPP or cc-pVTZ-F12 for MP2-F12, CCSD-F12 etc., check results with def2-QZVPP or cc-pVQZ-F12.