SCF methods, basis sets, and integrals

Lecture III: Basis sets

Wim Klopper

Abteilung für Theoretische Chemie, Institut für Physikalische Chemie
Karlsruher Institut für Technologie (KIT)

ESQC 2019, 8–21 September 2019

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.

- `DMol`[3] and `SIESTA` are DFT programs that use numerical atomic orbitals.

- The basis sets used by `DMol`[3] are denoted Minimal, DN, DND, DNP, TNP. Also `SIESTA` uses multiple-zeta and polarisation functions.

- In these programs, DFT is only available in the local-density (LDA) and generalised gradient approximations (GGA). Hybrid functionals and Hartree–Fock are not available.

- 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

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

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

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 `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:
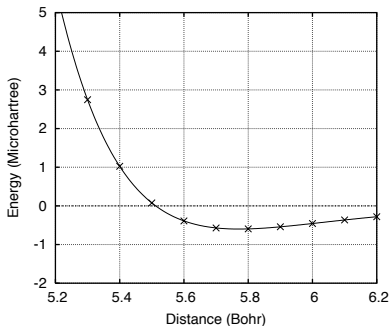
- The RHF/3-21G calculation of He$\cdots$He yields an interaction energy of $-0.6\ \mu E_\text{h}$ at $R = 5.77\ a_0$.

- 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. $-35\ \mu E_\text{h}$.

- The RHF/3-21G energy of the He atom is in error by $26\ \text{m}E_\text{h}$.

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.
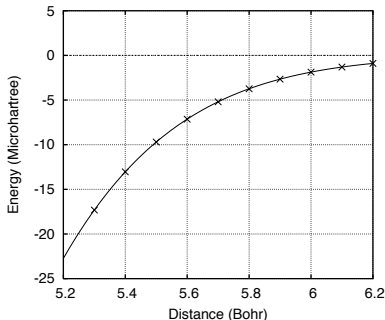
- Shown is the computed energy relative to the RHF calculation in only the atom's own 3-21G basis.

- This is the BSSE: artificial energy lowering due to neighbouring functions.

- At $R = 5.77\ a_0$, the artificial energy lowering is -4.1 μE_{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.

ΔE = **–** **–**

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

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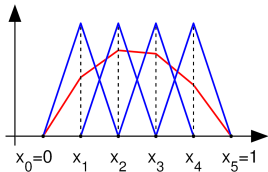
$$f(x) = \sum_{k=1}^{4} c_k \, f_k(x)$$

- 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$^{\text{nd}}$-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.
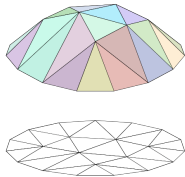
Wavelets

- 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,

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

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

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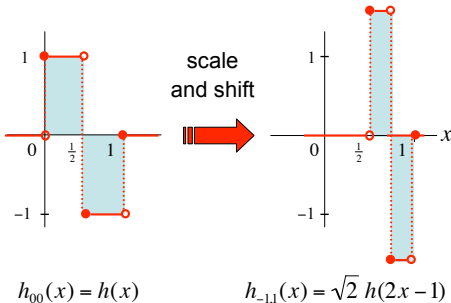
Plane (and spherical) waves

- Plane (and spherical) waves are used in DFT codes that treat the electronic structure of condensed matter.

Plane waves approach a small obstacle

Spherical waves propagate beyond the obstacle

- CPMD, FLEUR, VASP and Wien2K are programs using plane waves.
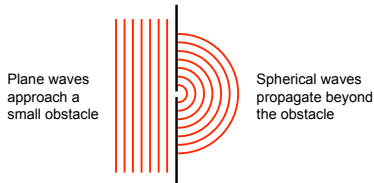
- The basis functions can be written as

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

- 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.

Augmented plane/spherical waves

- A second solution is to partition the unit cell into atomic spheres and the interstitial region and to use different basis functions for the two regions (augmented plane wave (APW) and augmented spherical wave (ASW) methods).

interstitial region   atomic spheres
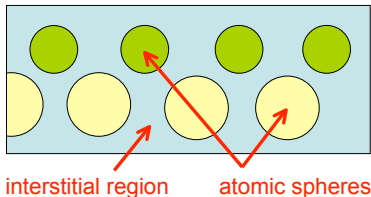
- The basis functions (the APWs) are constructed by matching the solutions of the Kohn–Sham equation inside each sphere with plane waves in the interstitial region.

- PPs can of course also be used in the APW and ASW methods.

Linear muffin-tin orbitals (LMTOs)

- The ASW and APW approaches are usually combined with the muffin-tin approximation to the potential.

- The muffin-tin potential is spherically symmetric inside non-overlapping atomic spheres and constant outside.

Full-potential (FP) approaches

- If the full potential is used in the place of the muffin-tin potential, the methods are denoted FP methods, for instance, FP-LAPW (also denoted FLAPW) or FP-LMTO.

$$V(\mathbf{r}) = \begin{cases} \sum_{lm} V_{\text{in}}^{lm}(r) Y_l^m(\vartheta, \varphi), & \text{inside the sphere} \\ \\ \sum_{\mathbf{G}} V_{\text{out}}^{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}, & \text{outside the sphere} \end{cases}$$

- The muffin-tin approximation means that the first sum is restricted to V_{in}^{00} and the second to $V_{\text{out}}^{\mathbf{0}}$.

- Adding local orbitals leads to the FP-LAPW-lo method, as for example implemented in the `FLEUR` and `Wien2K` programs.
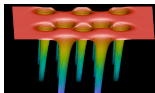
Actual self-consistent effective potential as obtained from an FLAPW calculation.

Hydrogen atom eigenfunctions
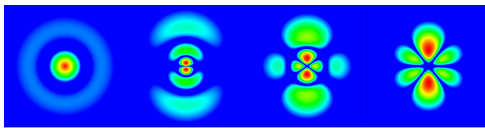
- The hydrogenic functions seem to form a natural basis for the MO-LCAO Ansatz.

- 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 (LF) form a complete, orthonormal set in the Hilbert space $L^2(\mathbb{R}^3)$.
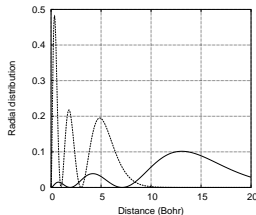
- The fig. shows radial distributions of the H-atom $3s$ (solid line) and the Laguerre function with $\zeta = 1$ (dashed).

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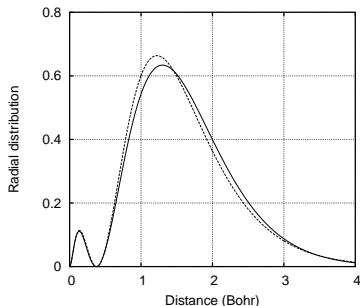
$$\varphi_{\mathrm{He}}(\mathbf{r}) = \sum_{n=1}^{n_{\max}} \sum_{k=1}^{k_{\max}(n)} c_{nk}\, r^{n-1} \exp(-\zeta_{nk} r)$$

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:

STO type	Exponents	Coefficients		
		$1s$	$2s$	$2p$
$1s$ 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 themselves 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

$$\varphi_{1s} \propto Rr, \qquad \left.\frac{\partial R(r)}{\partial r}\right|_{r=0} = -Z\,R(0) \neq 0$$
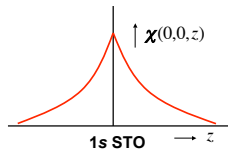
- STOs have the correct asymptotic long-range behaviour,

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

- Accurate calculations are possible for atoms and diatomics.

For Hartree–Fock calculations of atoms such as carbon, s- and p-type STOs are sufficient. For molecular calculations, also basis functions of symmetries that are not occupied in the atomic calculation must be considered.

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.
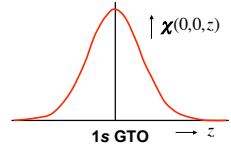
A program that uses STOs is `ADF`.

- 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.

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) $\rightarrow$ Course by Trond Saue

- 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 n 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 basis function (dashed line) replaces an STO with $\zeta = 1.24$ (solid line).
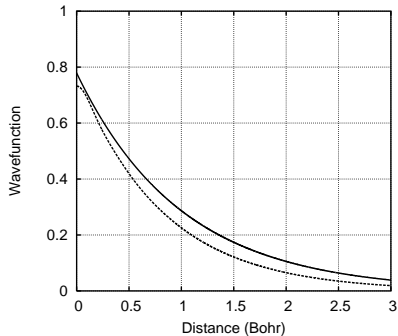

$\chi(r)$
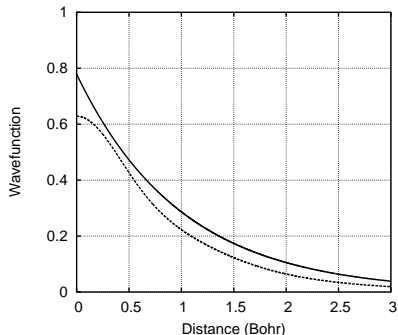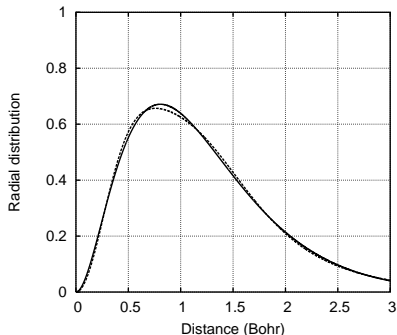
$4\pi\, r^2\, \chi^2(r)$

The figure on the left the STO-3G basis function has no cusp at $r = 0$.
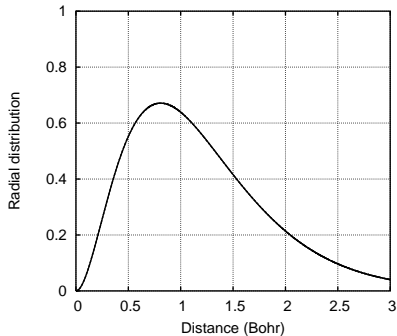The figure on the right shows that the radial distribution is already very well represented by 3 Gaussians.

STO-nG basis sets

The H-atom STO-6G basis 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 the STO-6G basis function has no cusp at $r = 0$.
The figure on the right shows that the two radial distributions are indistinguishable!

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'.

STO-nG basis sets

- The minimal basis (or single-zeta, SZ) basis has a single basis function for each orbital that is occupied in the atom.

- For example, the STO-3G minimal basis for bromium (configuration: [Ar]$3d^{10}4s^24p^5$) consists of the basis $4s3p1d$ with $4 + 3 \times 3 + 5 = 18$ functions.

STO-3G minimal basis

H – He:	$1s$
Li - Ne:	$2s1p$
Na - Ar:	$3s2p$
K, Ca:	$4s3p$
Sc – Kr:	$4s3p1d$
Rb, Sr:	$5s4p1d$
Y – I:	$5s4p2d$

- The basis sets in the table do not strictly follow the minimum-basis principle. For example, the basis for Ca does not require 3 sets of p-type functions.

- The STO-3G sets are usually used with five d-components (not six).

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.

- Large cores are used. In the 3-21G basis for Ga, the $[Ar]3d^{10}$ configuration is described by a minimal basis. A double-zeta sp-set is used to describe the $4s4p$ valence shell.

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 basis sets denoted as 6-31G** and SVP but they *are not* in basis sets denoted 6-31G* and SV(P).

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 (as computed by RPA, TD-DFT).

"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

'def2" sets from the `Turbomole` basis-set library

- The "def2" basis sets were tested for a set of ca. 300 molecules representing nearly each element in nearly all of its common oxidation states.

BaF, BaF_2, BaH_2, BaO, BaS, Be_2F_4, Be_2H_4, Be_4, BeC_2H_6, $BeF_2O_2H_4$, BeH_2, BeS, $CaCl_2$, CaF_2, CaH_2, CsF, CsH, CsO, K_2S, K_3P, KBr, KCl, KF, KH, KI,

Li_2, Li_2O, $Li_4C_4H_{12}$, Li_4Cl_4, Li_4H_4, Li_8, $LiBH_4$, $LiCl$, LiF, LiH, $LiSLi$, Mg_4, $MgCl_2$, MgF, MgF_2, MgH_2, Na_2O, Na_2S, Na_3N, Na_3P, $NaCl$, NaF, NaH, PLi_3,

RbF, RbH, RbO, SrF, SrF_2, SrH_2, SrO, SrS, B_2H_6, $B_3N_3H_6$, B_4H_4, BF_3, BH_3, BH_3CO, BH_3NH_3, C_2H_2, C_2H_3N, C_2H_4, C_2H_6, C_4H_4, C_6H_6, CF_4,

CH_2O, CH_2O_2, CH_3N, CH_3OH, CH_4, CO, CO_2, F_2, H_2, H_2CO_3, H_2O, H_2O_2, HCN, HF, HNC, HNO, HNO_2, HNO_3, N_2, N_2H_2, N_2H_4, N_4, NF_3, NH_3,

NH_4F, OF_2, Al_2O_3, Al_2S_3, $AlCl_3$, AlF_3, AlH_3, AlN, CS_2, Cl_2, ClF, ClF_3, H_2SO_4, H_3PO_4, HCP, HCl, H_2S, H_2S_2, P_2, PF_3, PF_5, PH_3, S_2, S_5, SF_2,

SF_4, SF_6, $SiCl_4$, SiF_4, SiH_4, SiO_2, SiS_2, As_4, As_4S_4, $AsCl_3$, $AsCl_6$, AsH_3, Br_2, $BrCl$, BrO_4, $GaCl$, $GaCl_3$, GaF, GaF_2, GaH_3, GaO, $GeCl_4$, GeF_3, GeF_4,

GeH_4, GeO, GeO_2, HBr, $HCBr_3$, Se_8, SeH_2, SeO, SeO_2, I_2, ICl, IH, IO_4, $InCl$, $InCl_3$, InH, InH_3, InO, $SbCl_6$, SbF, SbF_3, SbH_3, SbO_2, SnF_3, SnH_4, SnO,

SnO_2, TeF_3, TeH_2, TeO, TeO_2, XeF_2, XeF_4, $XeOF_4$, $BiCl_6$, BiF, BiF_3, BiH_3, BiO_2, PbF_3, PbH_4, PbO, PbO_2, $TlCl$, $TlCl_3$, TlH, TlH_3, TlO, $CoCl_2$, CoF_2,

CoF_3, $Cr(CO)_6$, $CrCl_3$, CrF_3, CrO_3, Cu_2, Cu_2O, Cu_2S, $CuCN$, $CuCl$, CuF, CuH, $Fe(CO)_5$, FeF_2, FeF_3, FeO, $Ferrocene$, MnF_2, MnO, MnO_2, MnO_3F, MnO_4,

MnS, $Ni(CO)_4$, $NiCl_2$, NiF_2, NiF_3, NiO, NiS, $ScCl_3$, ScF_3, ScH_3, ScO, $Ti(CO)_4$, $TiCl_4$, TiF_3, TiF_4, TiH_4, TiO, TiO_2, TiS_2, VH_5, VO, VOF_3, $ZnCl_2$, ZnF_2,

ZnH_2, $ZnMe_2$, Ag_2, $AgCl$, CdF_2, $CdMe_2$, $Mo(CO)_6$, MoF_3, MoH, MoO_2, MoO_3, NbF_3, NbO, NbO_2, NbO_2F, $Pd(CO)_4$, PdF, PdO_2, RhF, RhF_4, RhF_6, RhO,

$Ru(CO)_5$, RuF, RuO, RuO_2, RuO_4, Tc_2O_7, TcO, TcO_3F, YF, YF_3, YO, ZrF, ZrF_3, ZrO,

ZrO_2, Au_2, Au_3, $AuCl$, $AuCl_3$, HfF, HfF_3, HfO, HfO_2, Hg_2Cl_2, HgF_2, $HgMe_2$, IrF_6, $Os(CO)_5$, OsO_2, OsO_3, OsO_4, $OsOF_5$, $Pt(CO)_4$, PtO, PtO_2,

ReH, ReO, ReO_2, ReO_3, ReO_3F, TaF, TaF_3, TaO_2F, $W(CO)_6$, WF_3, WH, WO, WO_2, WO_3.

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.

- They 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, and a third s-type basis function with exponent 0.16058 a_0^{-2}.

Performance of various basis sets

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

- The DZP-type sets (SVP, 6-31G*, pc-1) perform similarly. So do the triple-zeta sets (cc-pVTZ, pc-2).

Ionization potentials (28):
Si, P, S, Cl, P$_2$, S$_2$, Cl$_2$, SiH$_2$, SiH$_3$, SiH$_4$, Si$_2$H$_2$, Si$_2$H$_4$, Si$_2$H$_5$, Si$_2$H$_6$, PH, PH$_2$, PH$_3$, HS, H$_2$S, CS, CS$_2$, CSO, H$_2$CS, HCl, ClF, CH$_3$SH, CH$_3$Cl, thiirane
Atomization energies (76), equilibrium distances (143) and frequencies (548):
Si$_2$, SiH, SiH$_2$ (singlet), SiH$_2$ (triplet), SiH$_3$, SiH$_4$, Si$_2$H$_2$, Si$_2$H$_4$, Si$_2$H$_5$, Si$_2$H$_6$, SiN, SiO, SiF$_4$, SiP, SiS, SiCl, SiCl$_2$, SiCl$_4$, CH$_3$SiH$_3$, vinyl-SiH$_3$, P$_2$, P$_4$, PH, PH$_2$, PH$_3$, PN, PO, PF$_3$, PS, PCl$_3$, Cl$_2$, POCl$_3$, CH$_3$PH$_2$, vinyl-PH$_2$, S$_2$, HS, H$_2$S, CS, CS$_2$, SN, SO, SO$_2$, SO$_3$, SF$_6$, SCl, SCl$_2$, S$_2$Cl$_2$, CSO, H$_2$CS, CH$_3$S, CH$_3$SH, vinyl-SH, (CH$_3$)$_2$S, (CH$_3$)$_2$SO, (CH$_3$)$_2$SO$_2$, thiirane, thiophene, Cl$_2$, HCl, ClN, ClO, ClF, ClF$_3$, HOCl, ClNO, CCl$_4$, C$_2$Cl$_4$, CH$_3$Cl, CH$_2$Cl$_2$, CHCl$_3$, CF$_3$Cl, Cl$_2$SO$_2$, vinyl-Cl, acetyl-Cl

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.

- The Karlsruhe "def2" sets have segmented contraction and are available for the atoms H–Rn ($Z = 86$).

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
BODC correction	≈ 0.0
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 ($\rightarrow$ Lectures by Jürgen Gauß).

- 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 sequences 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% of the correlation energy or more.

Ionisation potential (IP) of Ne and electron affinity (EA) of F

- We start with all-electron CCSD calculations in a very large d-aug-cc-pwCV5Z basis (217 functions).

- Results are shown in eV.

System	CCSD	Experiment
Ne IP	21.5054	21.5645
F EA	3.2276	3.4012

Ionisation potential (IP) of Ne and electron affinity (EA) of F

- We repeat the all-electron CCSD calculations using the d-aug-cc-pwCV5Z basis plus two-electron functions $\varphi_k(\mu)\varphi_l(\nu)\exp(-r_{\mu\nu})$ (CCSD(F12) model).

- Results are shown in eV.

System	CCSD	CCSD(F12)	Experiment
Ne IP	21.5054	21.5412	21.5645
F EA	3.2276	3.2490	3.4012

Ionisation potential (IP) of Ne and electron affinity (EA) of F

- Let us now move to the CCSDTQ5 level by performing the following calculations:
  - CCSD(T) in the d-aug-cc-pwCV5Z basis,
  - CCSDT(Q) in the d-aug-cc-pwCVQZ basis,
  - CCSDTQ in the d-aug-cc-pwCVTZ basis,
  - CCSDTQ5 in the d-aug-cc-pwCVDZ basis.

- Results are shown in eV.

System	CCSD(F12)	(T)	(T)→5	Best calc.	Experiment
Ne IP	21.5412	0.0788	−0.0027	21.6174	21.5645
F EA	3.2490	0.1821	−0.0028	3.4283	3.4012

Ionisation potential (IP) of Ne and electron affinity (EA) of F

- What else can be done?
  - We may compute the scalar relativistic effects.
  - The mass–velocity, the one-electron Darwin, and the two-electron Darwin energies were computed.
  - Level of theory: CCSD(T)/d-aug-cc-pwCV5Z.

- Results are shown in eV.

System	Previous best	Scalar rel.	Best calc.	Experiment
Ne IP	21.6173	−0.0175	21.5998	21.5645
F EA	3.4284	−0.0098	3.4186	3.4012

Ionisation potential (IP) of Ne and electron affinity (EA) of F

- What else can be done?
  - Ne^+ and F are open shell-systems!
  - Spin–orbit coupling will split the energy levels of these ions.
- Results are shown in eV.

System	Previous best	Spin–orbit	Best calc.	Experiment
Ne IP	21.5998	−0.0323	21.5675	21.5645
F EA	3.4186	−0.0167	3.4019	3.4012

Ionisation potential (IP) of Ne and electron affinity (EA) of F

- What else can be done?
  - We may compute higher-order scalar relativistic effects.
  - The Breit interaction and QED effects are added.
- Results are shown in eV.

System	Previous best	Breit + QED	Best calc.	Experiment
Ne IP	21.5675	–0.0025	21.5650	21.5645
F EA	3.4019	0.0001	3.4020	3.4012

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.