5 Basis Sets

Ab initio methods try to derive information by solving the Schrödinger equation without fitting parameters to experimental data. Actually, *ab initio* methods also make use of experimental data, but in a somewhat more subtle fashion. Many different approximate methods exist for solving the Schrödinger equation, and which one to use for a specific problem is usually chosen by comparing the performance against known experimental data. Experimental data thus guides the *selection* of the computational model, rather than directly *entering* into the computational procedure.

One of the approximations inherent in essentially all *ab initio* methods is the introduction of a basis set. Expanding an unknown function, such as a molecular orbital, in a set of known functions is not an approximation if the basis set is *complete*. However, a complete basis set means that an infinite number of functions must be used, which is impossible in actual calculations. An unknown MO can be thought of as a function in the infinite coordinate system spanned by the complete basis set. When a finite basis set is used, only the components of the MO along those coordinate axes corresponding to the selected basis functions can be represented. The smaller the basis set, the poorer the representation. The *type* of basis functions used also influence the accuracy. The better a single basis function is able to reproduce the unknown function, the fewer basis functions are necessary for achieving a given level of accuracy. Knowing that the computational effort of *ab initio* methods scales formally as at least M_{basis}^4, it is of course of prime importance to make the basis set as small as possible, without compromising the accuracy.[1] The expansion of the molecular orbitals leads to integrals of quantum mechanical operators over basis functions, and the ease with which these integrals can be calculated also depends on the type of basis function. In some cases the *accuracy-per-function* criterion produces a different optimum function type than the *efficiency-per-function* criterion.

5.1 Slater and Gaussian Type Orbitals

There are two types of basis functions (also called *Atomic Orbitals* (AO), although they in general are not solutions to an atomic Schrödinger equation) commonly used

in electronic structure calculations: *Slater Type Orbitals* (STO) and *Gaussian Type Orbitals* (GTO). Slater type orbitals[2] have the functional form shown in eq. (5.1).

$$\chi_{\zeta,n,l,m}(r,\theta,\varphi) = NY_{l,m}(\theta,\varphi)r^{n-1}e^{-\zeta r} \tag{5.1}$$

Here N is a normalization constant and $Y_{l,m}$ are spherical harmonic functions. The exponential dependence on the distance between the nucleus and electron mirrors the exact orbitals for the hydrogen atom. However, the STOs do not have any radial nodes; nodes in the radial part are introduced by making linear combinations of STOs. The exponential dependence ensures a fairly rapid convergence with increasing numbers of functions, however, as noted in Section 3.5, the calculation of three- and four-centre two-electron integrals cannot be performed analytically. STOs are primarily used for atomic and diatomic systems where high accuracy is required, and in semi-empirical methods where all three- and four-centre integrals are neglected. They can also be used with density functional methods that do not include exact exchange and where the Coulomb energy is calculated by fitting the density into a set of auxiliary functions.

Gaussian type orbitals[3] can be written in terms of polar or Cartesian coordinates as shown in eq. (5.2).

$$\chi_{\zeta,n,l,m}(r,\theta,\varphi) = NY_{l,m}(\theta,\varphi)r^{2n-2-l}e^{-\zeta r^2}$$

$$\chi_{\zeta,l_x,l_y,l_z}(x,y,z) = Nx^{l_x}y^{l_y}z^{l_z}e^{-\zeta r^2} \tag{5.2}$$

The sum of l_x, l_y and l_z determines the type of orbital (for example $l_x + l_y + l_z = 1$ is a p-orbital). Although a GTO appears similar in the two set of coordinates, there is a subtle difference. A d-type GTO written in terms of the spherical functions has five components ($Y_{2,2}$, $Y_{2,1}$, $Y_{2,0}$, $Y_{2,-1}$, $Y_{2,-2}$), but there appear to be six components in the Cartesian coordinates (x^2, y^2, z^2, xy, xz, yz). The latter six functions, however, may be transformed to the five spherical d-functions and one additional s-function ($x^2 + y^2 + z^2$). Similarly, there are ten Cartesian "f-functions" that may be transformed into seven spherical f-functions and one set of spherical p-functions. Modern programs for evaluating two-electron integrals are geared to Cartesian coordinates and they generate pure spherical d-functions by transforming the six Cartesian components to the five spherical functions. When only one d-function is present per atom the saving by removing the extra s-function is small, but if many d-functions and/or higher angular momentum functions (f-, g-, h-, etc., functions) are present, the saving can be substantial. Furthermore, the use of only the spherical components reduces the problems of linear dependence for large basis sets, as discussed below.

The r^2 dependence in the exponential makes the GTOs inferior to the STOs in two respects. At the nucleus a GTO has a zero slope, in contrast to a STO which has a "cusp" (discontinuous derivative), and GTOs consequently have problems representing the proper behaviour near the nucleus. The other problem is that the GTO falls off too rapidly far from the nucleus compared with an STO, and the "tail" of the wave function is consequently represented poorly. Both STOs and GTOs can be chosen to form a complete basis, but the above considerations indicate that more GTOs are necessary for achieving a certain accuracy compared with STOs. A rough guideline says that three times as many GTOs as STOs are required for reaching a given level of accuracy. Figure 5.1 shows how a 1s-STO can be modelled by a linear combination of three GTOs.
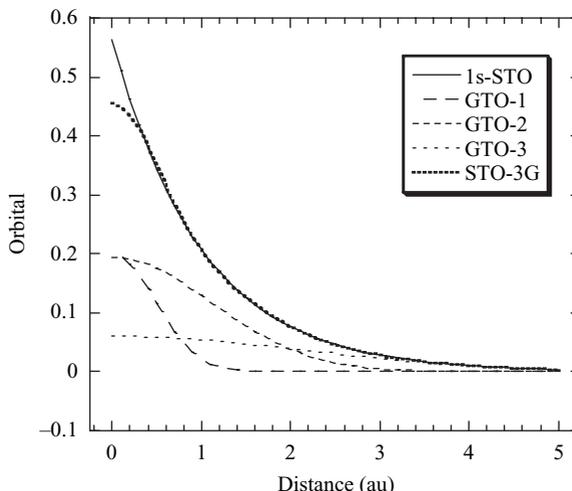
Figure 5.1   A 1s-STO modelled by a linear combination of three GTOs (STO-3G)

The increase in the number of GTO basis functions, however, is more than compensated for by the ease of which the required integrals can be calculated. In terms of computational efficiency, GTOs are therefore preferred and are used almost universally as basis functions in electronic structure calculations. Furthermore, essentially all applications take the GTOs to be centred at the nuclei. For certain types of calculations the centre of a basis function may be taken not to coincide with a nucleus, for example being placed at the centre of a bond or between non-bonded atoms for improving the calculation of van der Waals interactions.

5.2   Classification of Basis Sets

Having decided on the type of function (STO/GTO) and the location (nuclei), the most important factor is the number of functions to be used. The smallest number of functions possible is a *minimum basis set*. Only enough functions are employed to contain all the electrons of the neutral atom(s). For hydrogen (and helium) this means a single *s*-function. For the first row in the periodic system it means two *s*-functions (1s and 2s) and one set of *p*-functions ($2p_x$, $2p_y$ and $2p_z$). Lithium and beryllium formally only require two *s*-functions, but a set of *p*-functions is usually also added. For the second row elements, three *s*-functions (1s, 2s and 3s) and two sets of *p*-functions (2p and 3p) are used.

The next improvement of the basis sets is a doubling of all basis functions, producing a *Double Zeta* (DZ) type basis. The term zeta stems from the fact that the exponent of STO basis functions is often denoted by the Greek letter ζ. A DZ basis thus employs two *s*-functions for hydrogen (1s and 1s′), four *s*-functions (1s, 1s′, 2s and 2s′) and two sets of *p*-functions (2p and 2p′) for first row elements, and six *s*-functions and four sets of *p*-functions for second row elements. The importance of a DZ over a minimum basis can be illustrated by considering the bonding in the HCN molecule. The H—C bond will primarily consist of the hydrogen s-orbital and the p_z-orbital on C.

The π-bond between C and N will consist of the p_x (and p_y) orbitals of C and N, and will have a more diffuse electron distribution than the H—C σ-bond. The optimum exponent for the carbon p-orbital will thus be smaller for the x-direction than for the z-direction. If only a single set of p-orbitals is available (minimum basis), a compromise will be necessary. A DZ basis, however, has two sets of p-orbitals with different exponents. The tighter function (larger exponent) can enter the H—C σ-bond with a large coefficient, while the more diffuse function (small exponent) can be used primarily for describing the C—N π-bond. Doubling the number of basis functions thus allows for a much better description of the fact that the electron distribution is different in different directions.
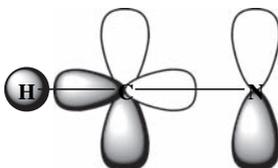
Figure 5.2   A double zeta basis allows for different bonding in different directions

The chemical bonding occurs between valence orbitals. Doubling the 1s-functions in for example carbon allows for a better description of the 1s-electrons. However, the 1s-orbital is essentially independent of the chemical environment, being very close to the atomic case. A variation of the DZ type basis only doubles the number of valence orbitals, producing a *split valence basis*. In actual calculations, a doubling of the core orbitals would rarely be considered, and the term DZ basis is used also for split valence basis sets (or sometimes VDZ, for valence double zeta).

The next step up in basis set size is a *Triple Zeta* (TZ). Such a basis contains three times as many functions as the minimum basis, i.e. six *s*-functions and three *p*-functions for the first row elements. Some of the core orbitals may again be saved by only splitting the valence, producing a *triple split valence* basis set. Again the term TZ is used to cover both cases. The names *Quadruple Zeta* (QZ) and *Quintuple* or *Pentuple Zeta* (PZ or 5Z, but not QZ) for the next levels of basis sets are also used, but large basis sets are often given explicitly in terms of the number of basis functions of each type.

So far, only the number of *s*- and *p*-functions for each atom (first or second row in the periodic table) has been discussed. In most cases, higher angular momentum functions are also important, and these are denoted *polarization functions*. Consider again the bonding in HCN in Figure 5.2. The H—C bond is primarily described by the hydrogen s-orbital(s) and the carbon s- and p_z-orbitals. It is clear that the electron distribution *along* the bond will be different than *perpendicular* to the bond. If only *s*-functions are present on hydrogen, this cannot be described. However, if a set of p-orbitals is added to hydrogen, the p_z component can be used for improving the description of the H—C bond. The p-orbital introduces a polarization of the s-orbital(s). Similarly, d-orbitals can be used for polarizing p-orbitals, f-orbitals for polarizing d-orbitals, etc. Once a p-orbital has been added to polarize a hydrogen s-orbital, it may be argued that the p-orbital should now be polarized by adding a d-orbital, which should be polarized by an f-orbital, etc. For independent-particle wave functions, where electron correlation is not considered, the first set of polarization functions (i.e. *p*-functions for

hydrogen and *d*-functions for heavy atoms) is by far the most important, and will in general describe most of the important charge polarization effects.

If methods including electron correlation are used, higher angular momentum functions are essential. Electron correlation describes the energy lowering by the electrons "avoiding" each other, beyond the average effect taken into account by Hartree–Fock methods. Two types of correlation can be identified, an "*in–out*" and an "*angular*" correlation. The in-out or *radial correlation* refers to the situation where one electron is close to, and the other far from, the nucleus. To describe this, the basis set needs functions of the same type, but with different exponents. The *angular correlation* refers to the situation where two electrons are on opposite sides of the nucleus. To describe this, the basis set needs functions with the same magnitude exponents, but different angular momentum. For example, to describe angular correlation of an *s*-function, *p*-functions (and *d*-, *f*-, *g*-functions, etc.) are needed. The angular correlation is of similar importance as the radial correlation, and higher angular momentum functions are consequently essential for correlated calculations. Although these should properly be labelled correlation functions, they also serve as polarization functions for HF wave functions, and it is common to denote them as polarization functions.

Normally only the correlation of the valence electrons is considered, and the exponents of the polarization functions should be of the same magnitude as the valence *s*- and *p*-functions (actually slightly larger in order to have the same maximum in the radial distribution function). In contrast to HF methods, the higher angular momentum functions (beyond the first set of polarization functions) are quite important. Or alternatively formulated, the convergence in terms of angular momentum is slower for correlated wave functions than at the HF level. For a basis set that is complete up to angular momentum L, numerical analysis suggests the asymptotic convergence at the HF level is exponential (i.e. $\sim\exp(-\sqrt{L})$), while it is $\sim L^{-3}$ at correlated levels.[4]

Polarization functions are added to the chosen *sp*-basis. Adding a single set of polarization functions (*p*-functions on hydrogens and *d*-functions on heavy atoms) to the DZ basis forms a *Double Zeta plus Polarization* (DZP) type basis. There is a variation where polarization functions are only added to non-hydrogen atoms. This does not mean that polarization functions are not important on hydrogen. However, hydrogen often has a "passive" role, sitting at the end of bonds that do not take active part in the property of interest. The error introduced by not including hydrogen polarization functions is often rather constant and, as the interest is usually in energy differences, tends to cancel out. As hydrogen often accounts for a large number of atoms in the system, a saving of three basis functions for each hydrogen is significant. If hydrogen plays an important role in the property of interest, it is of course not a good idea to neglect polarization functions on hydrogen.

Similarly to the *sp*-basis sets, multiple sets of polarization functions with different exponents may be added. If two sets of polarization functions are added to a TZ *sp*-basis, a *Triple Zeta plus Double Polarization* (TZ2P) type basis is obtained. For larger basis sets with many polarization functions the explicit composition in terms of number and types of functions is usually given. At the HF level there is usually little gained by expanding the basis set beyond TZ2P, and even a DZP type basis set usually gives "good" results (compared with the HF limit). Correlated methods, however, require more, and higher angular momentum, polarization functions to achieve the same level of convergence.

Before moving on we need to introduce the concept of *basis set balance*. In principle, many sets of polarization functions may be added to a small *sp*-basis, but this is a poor idea. If an insufficient number of *sp*-functions has been chosen for describing the fundamental electron distribution, the optimization procedure used in obtaining the wave function (and possibly also the geometry) may try to compensate for inadequacies in the *sp*-basis by using higher angular momentum functions, thereby producing artefacts. A rule of thumb says that the number of functions of a given type should at most be one less than the type with one lower angular momentum. A 3s2p1d basis is balanced, but a 3s2p2d2f1g is too heavily polarized. It may not be necessary to polarize the basis all the way up, thus a 5s4p3d2f1g basis is balanced, but if it is known (for example by comparison with experimental data) that *f*- and *g*-functions are unimportant, they may be left out. Furthermore, it may be that two *d*-functions are sufficient for the given purpose, although a 5s4p1d basis would be considered underpolarized.

Another aspect of basis set balance is the occasional use of *mixed* basis sets, for example a DZP quality on the atoms in the "interesting" part of the molecule and a minimum basis for the "spectator" atoms. Another example would be the addition of polarization functions for only a few hydrogens that are located "near" the reactive part of the system. For a large molecule, this may lead to a substantial saving in the number of basis functions. It should be noted that this may bias the results and can create artefacts. For example, a calculation on the H_2 molecule with a minimum basis at one end and a DZ basis at the other end will predict that H_2 has a dipole moment, since the variational principle will preferentially place the electrons near the centre with the most basis functions. The majority of calculations are therefore performed with basis sets of the same quality (minimum, DZP, TZ2P, . . .) on all atoms, possibly removing polarization and/or diffuse (small exponent) functions on hydrogen. Even so, it may be argued that small basis sets inherently tend to be unbalanced. Consider for example the LiF molecule in a minimum or DZ type basis. This will have a very ionic structure, Li^+F^-, with nearly all the valence electrons being located at the fluorine. In terms of number of basis functions per electron, the Li basis is thus of a much higher quality than the F basis, and thereby unbalanced. This effect of course diminishes as the size of the atomic basis set increases.

Except for very small systems, it is impractical to saturate the basis set such that the absolute error in the energy is reduced below chemical accuracy, say 4 kJ/mol. The important point in choosing a balanced basis set is to keep the error as constant as possible. The use of mixed basis sets should therefore only be done after careful consideration. Furthermore, the use of small basis sets for systems containing elements with substantially different numbers of valence electrons (such as LiF) may produce artefacts.

Having decided on the number of basis functions (from a consideration of the property of interest and the computational cost), the question becomes: how are the values for the exponents in the basis functions chosen? The values for the *s*- and *p*-functions are typically determined by performing variational HF calculations for the atoms, using the exponents as variational parameters. The exponent values that give the lowest energy are the "best", at least for the atom. In some cases, the optimum exponents are chosen based on minimizing the energy of a wave function that includes electron correlation. The HF procedure cannot be used for determining exponents of polarization

functions for atoms. By definition these functions are unoccupied in atoms, and therefore make no contribution to the energy. Suitable polarization exponents may be chosen by performing variational calculations on molecular systems (where the HF energy does depend on polarization functions) or on atoms with correlated wave functions. Since the main function of higher angular momentum functions is to recover electron correlation, the latter approach is usually preferred. Often only the optimum exponent is determined for a single polarization function, and multiple polarization functions are generated by splitting the exponents symmetrically around the optimum value for a single function. The splitting factor is typically taken in the range 2–4. For example if a single d-function for carbon has an exponent value of 0.8, two polarization functions may be assigned with exponents of 0.4 and 1.6 (splitting factor of 4). The details of how the exponents are determined for various basis sets are discussed in the following sections.

5.3   Even- and Well-Tempered Basis Sets

The optimization of basis function exponents is an example of a highly non-linear optimization problem (Chapter 12). When the basis set becomes large, the optimization problem is no longer easy. The basis functions start to become linearly dependent (the basis set approaches completeness) and the energy becomes a very flat function of the exponents. Analyses of basis sets that have been optimized by variational methods reveal that the ratio between two successive exponents is approximately constant. Taking this ratio to be constant reduces the optimization problem to only two parameters for each type of basis function, *independent of the size of the basis*. Such basis sets have been labelled *even-tempered* basis sets, with the ith exponent given as $\zeta_i = \alpha\beta^i$, where α and β are fixed constants for a given type of function and nuclear charge. It was later discovered that the *optimum* α and β constants to a good approximation can be written as functions of the size of the basis set, M.[5]

$$\zeta_i = \alpha\beta^i; \quad i = 1, 2, \ldots, M$$
$$\ln(\ln\beta) = b\ln M + b' \tag{5.3}$$
$$\ln\alpha = a\ln(\beta - 1) + a'$$

The constants a, a', b and b' depend only on the atom type and the type of function (s or p). Even-tempered basis sets have the advantage that it is easy to generate a sequence of basis sets that are guaranteed to converge towards a complete basis. This is useful if the attempt is to extrapolate a given property to the basis set limit. The disadvantage is that the convergence is somewhat slow, and an explicitly optimized basis set of a given size will usually give a better answer than an even-tempered basis of the same size.

Even-tempered basis sets have the same ratio between exponents over the whole range. From chemical considerations it is usually preferable to cover the valence region better than the core region. This may be achieved by *well-tempered* basis sets.[6] The idea is similar to the even-tempered basis sets, with the exponents being generated by a suitable formula containing only a few parameters to be optimized. The exponents in a well-tempered basis of size M are generated according to eq. (5.4).

$$\zeta_i = \alpha\beta^{i-1}\left(1 + \gamma\left(\frac{i}{M}\right)^\delta\right); \quad i = 1, 2, \ldots, M \tag{5.4}$$

The α, β, γ and δ parameters are optimized for each atom. The exponents are the same for all types of angular momentum functions, and s-, p- and d-functions (and higher angular momentum) consequently have the same radial part.

A well-tempered basis set has four parameters, compared with two for an even-tempered one, and is consequently capable of giving a better result for the same number of functions. Petersson *et al.*[7] have proposed a somewhat more general parameterization based on expanding the logarithmic exponents in a polynomial of order K in the basis function number.

$$\ln\zeta_i = \sum_{k=0}^{K} a_k i^k; \quad i = 1, 2, \ldots, M \tag{5.5}$$

Setting $K = 1$ is equivalent to generating an even-tempered basis set. The optimization of the parameters a_k becomes problematic for K larger than 2, since the polynomials are non-orthogonal, and increasing K thus significantly changes all the expansion coefficients. This problem can be alleviated by using *Legendre* polynomials instead, since these are orthogonal, and this significantly improves the optimization.

$$\begin{aligned}
\ln\zeta_i &= \sum_{k=0}^{K} a_k P_k(i); \quad i = 1, 2, \ldots, M \\
P_0(i) &= 1 \\
P_1(i) &= i \\
P_2(i) &= i^2 - 1 \\
P_3(i) &= i^3 - i \\
&\ldots
\end{aligned} \tag{5.6}$$

It has been found that a fourth-order polynomial ($K = 3$) expansion produces much better results than the well-tempered formula, despite having the same number of variables. Furthermore, the results from a fourth-order Legendre parameterization with M basis functions is comparable to those from a fully optimized basis set with $M - 1$ functions, i.e. the penalty in reducing the number of optimization variables from M to four is only one function. The Legendre parameterization furthermore solves the potential problem of variational collapse, i.e. two neighbouring exponents collapsing to the same value during optimization, and eq. (5.6) thus provides an efficient way of systematically approaching the basis set limit.

Optimization of basis sets is not something the common user needs to worry about. Optimized basis sets of many different sizes and qualities are available either in the forms of tables, websites[8] or stored internally in the computer programs. The user "merely" has to select a suitable basis set. However, if the interest is in specialized properties the basis set may need to be tailored to meet the specific needs. For example if the property of interested is an accurate value for the electron density *at* the nucleus (for example for determining the Fermi contact contribution to spin–spin coupling (see Section 10.7.6)) then basis functions with very large exponents are required.

Alternatively, for calculating hyperpolarizabilites, very diffuse functions are required. In such cases, the basis function optimization is in terms of the property of interest, and not in terms of energy, i.e. basis functions are added until the change upon addition of one extra function is less than a given threshold.

5.4   Contracted Basis Sets

One disadvantage of all energy-optimized basis sets is the fact that they primarily depend on the wave function in the region of the inner-shell electrons. The 1s-electrons account for a large part of the total energy, and minimizing the energy will tend to make the basis set optimum for the core electrons, and less so for the valence electrons. However, chemistry is mainly dependent on the valence electrons. Furthermore, many properties (for example polarizability) depend mainly on the wave function "tail" (far from the nucleus), which energetically is unimportant. An energy-optimized basis set that gives a good description of the outer part of the wave function therefore needs to be very large, with the majority of the functions being used to describe the 1s-electrons with an accuracy comparable with the outer electrons in an energetic sense. This is not the most efficient way of designing basis sets for describing the outer part of the wave function. Instead energy-optimized basis set are usually augmented explicitly with *diffuse* functions (basis functions with small exponents). Diffuse functions are needed whenever loosely bound electrons are present (for example anions or excited states) or when the property of interest is dependent on the wave function tail (for example polarizability).

The fact that many basis functions focus on describing the energetically important, but chemically unimportant, core electrons is the foundation for *contracted* basis sets. Consider for example a basis set consisting of ten *s*-functions (and some *p*-functions) for carbon. Having optimized these ten exponents by a variational calculation on a carbon atom, maybe six of the ten functions are found primarily to be used for describing the 1s-orbital, and two of the four remaining describe the "inner" part of the 2s-orbital. The important chemical region is the outer valence. Out of the ten functions, only two are actually used for describing the chemically interesting phenomena. Considering that the computational cost increases as the fourth power (or higher) of the number of basis functions, this is inefficient. As the core orbitals change very little depending on the chemical bonding situation, the MO expansion coefficients in front of these inner basis functions also change very little. The majority of the computational effort is therefore spent describing the chemically uninteresting part of the wave function, which is furthermore almost constant.

Consider now making the variational coefficients in front of the inner basis functions constant, i.e. they are no longer parameters to be determined by the variational principle. The 1s-orbital is thus described by a *fixed* linear combination of say six basis functions. Similarly, the remaining four basis functions may be contracted into only two functions, for example by fixing the coefficient in front of the inner three functions. In doing this the number of basis functions to be handled by the variational procedure has been reduced from ten to three.

Combining the full set of basis functions, known as the *primitive* GTOs (PGTOs), into a smaller set of functions by forming fixed linear combinations is known as

basis set *contraction*, and the resulting functions are called *contracted* GTOs (CGTOs).

$$\chi(\text{CGTO}) = \sum_i^k a_i \chi_i(\text{PGTO}) \tag{5.7}$$

The previously introduced acronyms DZP, TZ2P, etc., refer to the number of contracted basis functions. Contraction is especially useful for orbitals describing the inner (core) electrons, since they require a relatively large number of functions for representing the wave function cusp near the nucleus, and furthermore are largely independent of the environment. Contracting a basis set will always increase the energy, since it is a restriction of the number of variational parameters, and makes the basis set less flexible, but it will also reduce the computational cost significantly. The decision is thus how much loss in accuracy is acceptable compared with the gain in computational efficiency.

The *degree of contraction* is the number of PGTOs entering the CGTO, typically varying between one and ten. The specification of a basis set in terms of primitive and contracted functions is done by the notation (10s4p1d/4s1p) → [3s2p1d/2s1p]. The basis in parenthesis is the number of primitives with heavy atoms (first row elements) before the slash and hydrogen after. The basis in the square brackets is the number of contracted functions. Note that this does not indicate how the contraction is done, it only indicates the size of the final basis (and thereby the size of the variational problem in HF calculations).

There are two different ways of contracting a set of primitive GTOs to a set of contracted GTOs: *segmented* and *general* contraction. Segmented contraction is the older method, and the one used in the above example. A given set of PGTOs is partitioned into smaller sets of functions that are made into CGTOs by determining suitable coefficients. A 10s basis set may be contracted to 3s by taking the inner six functions as one CGTO, the next three as the second CGTO and the one remaining PGTO as the third "contracted" GTO.

$$\chi_1(\text{CGTO}) = \sum_{i=1}^{6} a_i \chi_i(\text{PGTO})$$

$$\chi_{21}(\text{CGTO}) = \sum_{i=7}^{9} a_i \chi_i(\text{PGTO}) \tag{5.8}$$

$$\chi_3(\text{CGTO}) = \chi_{10}(\text{PGTO})$$

In a segmented contraction each primitive as a rule is used only in *one* contracted function, i.e. the primitive set of functions is partitioned into disjoint sets. In some cases it may be necessary to duplicate one or two PGTOs in two adjacent CGTOs. The contraction coefficients can be determined by a variational optimization of the atomic HF energy, where both the exponents and contraction coefficients are optimized simultaneously. It should be noted that this optimization often produces multiple minima, and selecting a suitable "optimum" solution may be non-trivial.[9]

In a general contraction *all* primitives (on a given atom) enter *all* the contracted functions, but with different contraction coefficients.

$$\chi_1(\text{CGTO}) = \sum_{i=1}^{10} a_i \chi_i(\text{PGTO})$$

$$\chi_{21}(\text{CGTO}) = \sum_{i=1}^{10} b_i \chi_i(\text{PGTO}) \tag{5.9}$$

$$\chi_3(\text{CGTO}) = \sum_{i=1}^{10} c_i \chi_i(\text{PGTO})$$

One popular way of obtaining general contraction coefficients is from *Atomic Natural Orbitals* (ANOs), to be discussed in Section 5.4.5. The difference between segmented and general contraction may be illustrated as shown in Figure 5.3.

	Segmented contraction			General contraction		
	CGTO-1	CGTO-2	CGTO-3	CGTO-1	CGTO-2	CGTO-3
PGTO-1						
PGTO-2						
PGTO-3						
PGTO-4						
PGTO-5						
PGTO-6						
PGTO-7						
PGTO-8						
PGTO-9						
PGTO-10						

Figure 5.3   Illustrating segmented and general contraction

In reality, there are very few truly segmented or general contracted basis sets. General contracted basis sets normally leave the outermost function(s) uncontracted, and a Gram–Schmidt type orthogonalization can be used for partly segmenting the inner functions.[10] The disjoint nature of the primitive set of functions in a segmented contraction, on the other hand, often necessitates a duplication of one or more functions, i.e. effectively a general contraction. The segmented–general classification should thus be seen as limiting cases, with actual basis sets having varying characteristics of both types.

There are many different contracted basis sets available in the literature or built into programs, and the average user usually only needs to select a suitable quality basis for the calculation. Below is a short description of some basis sets that often are used in routine calculations. The contractions are given for a first row element (such as carbon), while the corresponding ones for other elements can be found in the references.

5.4.1   Pople style basis sets

STO-nG basis sets   These are *Slater type orbitals* consisting of n PGTOs.[11] This is a minimum type basis where the exponents of the PGTO are determined by *fitting* to the STO, rather than optimizing them by a variational procedure. Although basis sets with $n = 2$–6 have been derived, it has been found that using more than three PGTOs for representing the STO gives little improvement, and the STO-3G basis is a widely used minimum basis. This type of basis set has been determined for many elements of the periodic table. The designation of the carbon STO-3G basis is (6s3p) → [2s1p].

k-nlmG basis sets　　These basis sets, designed by Pople and coworkers, and are of the split valence type, with the *k* in front of the dash indicating how many PGTOs are used for representing the core orbitals. The *nlm* after the dash indicate both how many functions the valence orbitals are split into, and how many PGTOs are used for their representation. Two values (*nl*) indicate a split valence, while three values (*nlm*) indicate a triple split valence. The values *before* the G (for Gaussian) indicate the *s*- and *p*-functions in the basis; the polarization functions are placed *after* the G. These types of basis sets have the further restriction that the same exponent is used for both the *s*- and *p*-functions in the valence. This increases the computational efficiency, but of course decreases the flexibility of the basis set. The exponents and contraction coefficients have been optimized by variational procedures at the HF level for atoms.

3-21G　　This is a split valence basis, where the core orbitals are a contraction of three PGTOs, the inner part of the valence orbitals is a contraction of two PGTOs and the outer part of the valence is represented by one PGTO.[12] The designation of the carbon 3-21G basis is (6s3p) → [3s2p]. Note that the 3-21G basis contains the same number of primitive GTOs as the STO-3G, however, it is much more flexible as there are twice as many valence functions that can combine freely to make MOs.

6-31G　　This is also a split valence basis, where the core orbitals are a contraction of six PGTOs, the inner part of the valence orbitals is a contraction of three PGTOs and the outer part of the valence is represented by one PGTO.[13] The designation of the carbon 6-31G basis is (10s4p) → [3s2p]. In terms of contracted basis functions it contains the same number as 3-21G, but the representation of each function is better since more PGTOs are used.

6-311G　　This is a triple split valence basis, where the core orbitals are a contraction of six PGTOs and the valence split into three functions, represented by three, one and one PGTOs, respectively, i.e. (11s5p) → [4s3p].[14]

To each of these basis sets can be added diffuse[15] and/or polarization functions.[16] Diffuse functions are normally *s*- and *p*-functions and consequently go before the G. They are denoted by + or ++, with the first + indicating one set of diffuse *s*- and *p*-functions on heavy atoms, and the second + indicating that a diffuse *s*-function is added also to hydrogen. The argument for only adding diffuse functions on non-hydrogen atoms is the same as for only adding polarization functions on non-hydrogens (Section 5.2). Polarization functions are indicated after the G, with a separate designation for heavy atoms and hydrogen. The 6-31+G(d) is a split valence basis with one set of diffuse *sp*-functions on heavy atoms only and a single *d*-type polarization function on heavy atoms. A 6-311++G(2df,2pd) is similarly a triple split valence with additional diffuse *sp*-functions, two *d*-functions and one *f*-function on heavy atoms, and diffuse *s*- and two *p*- and one *d*-functions on hydrogen. The largest standard Pople style basis set is 6-311++G(3df,3pd). These types of basis set have been derived for hydrogen and the first row elements, and some of the basis sets have also been derived for second and higher row elements. The composition in terms of contracted and primitive functions is given in Table 5.1.

　　If only one set of polarization functions is used, an alternative notation in terms of * is also widely used. The 6-31G* basis is identical to 6-31G(d), and 6-31G** is identical to 6-31G(d,p). A special note should be made for the 3-21G* basis. The 3-21G

Table 5.1 Composition in terms of contracted and primitive basis functions for some Pople style basis sets

Basis	Hydrogen		First row elements		Second row elements	
	Contracted	Primitive	Contracted	Primitive	Contracted	Primitive
STO-3G	1s	3s	2s1p	6s3p	3s2p	9s6p
3-21G	2s	3s	3s2p	6s3p	4s3p	9s6p
6-31G(d,p)	2s1p	4s	3s2p1d	10s4p	4s3p1d	16s10p
6-311G(2df,2pd)	3s2p1d	5s	4s3p2d1f	11s5p	6s4p2d1f[a]	13s9p[a]

[a] McLean–Chandler basis set

basis is basically too small to support polarization functions (it become unbalanced). However, the 3-21G basis by itself performs poorly for hypervalent molecules, such as sulfoxides and sulfones. This can be improved substantially by adding a set of *d*-functions. The 3-21G* basis has only *d*-functions on second row elements (it is sometimes denoted 3-21G(*) to indicate this), and should not be considered a polarized basis. Rather the addition of a set of *d*-functions is an *ad hoc* repair of a known flaw.

5.4.2 Dunning–Huzinaga basis sets

Huzinaga has determined uncontracted energy-optimized basis sets up to (10s6p) for first row elements.[17] This was latter extended to (14s9p) by van Duijneveldt,[18] and up to (18s13p) by Partridge.[19] Dunning has used the Huzinaga primitive GTOs to derive various contraction schemes, and these are known as Dunning–Huzinaga (DH) type basis sets.[20] A DZ type basis can be made by a contraction of the (9s5p) PGTO to [4s2p]. The contraction scheme is 6,1,1,1 for *s*-functions and 4,1 for the *p*-functions. A widely used split valence type basis is a contraction of the same primitive set to [3s2p] where the *s*-contraction is 7,2,1 (note that one primitive enters twice). A widely used TZ type basis (actually only a triple split valence) is a contraction of the (10s6p) to [5s3p], with the contraction scheme 6,2,1,1,1 for *s*-functions and 4,1,1 for *p*-functions. Again, a duplication of one of the *s*- and *p*-primitives has been allowed.

McLean and Chandler have developed a similar set of contracted basis sets from Huzinaga primitive optimized sets for second row elements.[21] A DZ type basis is derived by contracting (12s8p) → [5s3p], and a TZ type is derived by contracting (12s9p) → [6s5p]. The latter contraction is 6,3,1,1,1,1 for the *s*-functions (note a duplication of one function) and 4,2,1,1,1 for the *p*-functions, and is often used in connection with the Pople 6-311G when second row elements are present.

The Dunning–Huzinaga type basis sets do not have the restriction of the Pople style basis sets of equal exponents for the *s*- and *p*-functions, and they are therefore somewhat more flexible, but computationally also more expensive. The major determining factor, however, is the *number* of basis functions and less so the exact *description* of each function. Normally there is little difference in the performance between different DZ or different TZ type basis sets.

The primary reason for the popularity of the Pople and DH style basis sets is the extensive calibration available. There have been so many calculations reported with these basis sets that it is possible to get a fairly good idea of the level of accuracy that

can be attained with a given basis. This is of course a self-sustaining procedure, the more calculations that are reported with a given basis, the more popular it becomes, since the calibration set becomes larger and larger.

5.4.3 MINI, MIDI and MAXI basis sets

Tatewaki and Huzinaga have optimized minimum basis sets for a large part of the periodic table at the HF level.[22] The MINI-n ($n = 1$–4) basis sets are all minimum basis sets with three PGTOs in the 2s CGTO, and a varying number of PGTOs in the 1s and 2p CGTOs. In terms of PGTOs, the MINI-1 is (3s,3s,3p), the MINI-2 is (3s,3s,4p), the MINI-3 is (4s,3s,3p) and the MINI-4 is (4s,3s,4p). These MINI basis sets in general perform better than STO-3G, but it should be kept in mind that they are still minimum basis sets. The MIDI-n basis sets are identical to MINI-n, except that the outer valence function is decontracted. The MAXI-n basis sets all employ four PGTOs for the 2s CGTO and from five to seven PGTOs for the 1s and 2p CGTOs. The valence orbitals are split into three or four functions, and MAXI-1 is (9s5p) $\rightarrow$ [4s3p] (contraction 5,2,1,1 and 3,1,1), MAXI-3 is (10s6p) $\rightarrow$ [5s4p] (contraction 6,2,1,1,1 and 3,1,1,1) and MAXI-5 is (11s7p) $\rightarrow$ [5s4p] (contraction 7,2,1,1,1 and 4,1,1,1).

5.4.4 Ahlrichs type basis sets

The group centred around R. Ahlrichs has designed basis sets of DZ, TZ and QZ quality for the elements up to Kr. The *Split Valence Polarized* (SVP) basis set is a [3s2p] contraction of a (7s4p) set of primitive functions (contraction 5,1,1 and 3,1), while the *Triple Zeta Valence* (TZV) basis set is a [5s3p] contraction of an (11s6p) set of primitive functions (contraction 6,2,1,1,1 and 4,1,1).[23] More recently, the series has been extended by a *Quadruple Zeta Valence* (QZV) basis set, being a [7s4p] contraction of a (15s8p) set of primitive functions with the contraction 8,2,1,1,1,1,1 and 5,1,1,1.[24] Note that both the TZV and QZV basis sets employ more contracted s-functions than indicated by the TZ and QZ acronyms. The s- and p-exponents and corresponding contraction coefficients are optimized at the HF level, while the polarization functions are taken from the cc-pVxZ basis sets.

Table 5.2 Composition in terms of contracted and primitive basis functions for the Ahlrichs type basis sets

Basis	Hydrogen		First row elements		Second row elements	
	Contracted	Primitive	Contracted	Primitive	Contracted	Primitive
SVP	2s1p	4s	3s2p1d	7s4p	4s3p1d	10s7p
TZV	3s2p1d	5s	5s3p2d1f	11s6p	5s4p2d1f	14s9p
QZV	4s3p2d1f	7s	7s4p3d2f1g	15s8p	9s6p4d2f1g	20s14p

5.4.5 Atomic natural orbital basis sets

All of the above basis sets are of the segmented contraction type. Modern contracted basis sets aimed at producing very accurate wave functions often employ a general

contraction scheme. The *Atomic Natural Orbitals* (ANO) and correlation consistent basis sets below are of the general contraction type.

The idea in the ANO type basis sets is to contract a large PGTO set to a fairly small number of CGTOs by using *natural orbitals* from a correlated calculation on the free atom, typically at the CISD level.[25] The natural orbitals are those that diagonalize the density matrix, and the eigenvalues are called *orbital occupation numbers* (see Section 9.5). The orbital occupation number is the number of electrons in the orbital. For an RHF wave function, ANOs would be identical to the canonical orbitals with occupation numbers of exactly 0 or 2. When a correlated wave function is used, however, the occupation number may have any value between 0 and 2. The ANO contraction selects the important combinations of the PGTOs from the magnitude of the occupation numbers. A large primitive basis, typically generated as an even-tempered sequence, may generate several different contracted basis sets by gradually lowering the selection threshold for the occupation number. The nice feature of the ANO contraction is that it more or less "automatically" generates balanced basis sets, e.g. for neon the ANO procedure generates the following basis set: [2s1p], [3s2p1d], [4s3p2d1f] and [5s4p3d2f1g]. Furthermore, in such a sequence the smaller ANO basis sets are true subsets of the larger, since the same set of primitive functions is used.

5.4.6 Correlation consistent basis sets

The primary disadvantage of ANO basis sets is that a very large number of primitive GTOs are necessary for converging towards the basis set limit. Dunning and coworkers have proposed a somewhat smaller set of primitives that yields comparable results to the ANO basis sets.[26] The *correlation consistent* (cc; the convention is to use lower case letters as the acronym, to distinguish it from coupled cluster (CC)) basis sets are geared towards recovering the correlation energy of the valence electrons. The name correlation consistent refers to the fact that the basis sets are designed such that functions that contribute similar amounts of correlation energy are included at the same stage, independent of the function type. For example, the first *d*-function provides a large energy lowering, but the contribution from a second *d*-function is similar to that from the first *f*-function. The energy lowering from a third *d*-function is similar to that from the second *f*-function and the first *g*-function. The addition of polarization functions should therefore be done in the order: 1d, 2d1f and 3d2f1g. An additional feature of the cc basis sets is that the energy error from the *sp*-basis should be comparable with (or at least not exceed) the correlation error arising from the incomplete polarization space, and the *sp*-basis therefore also increases as the polarization space is extended. The *s*- and *p*-basis set exponents are optimized at the HF level for the atoms, while the polarization exponents are optimized at the CISD level, and the primitive functions are contracted by a general contraction scheme using natural orbital coefficients.

Several different sizes of cc basis sets are available in terms of final number of contracted functions. These are known by their acronyms: cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z and cc-pV6Z (*correlation consistent polarized Valence Double/Triple/Quadruple/Quintuple/Sextuple Zeta*). The composition in terms of contracted and primitive (for the *s*- and *p*-part) functions is shown in Table 5.3. Note that each step up in terms of quality increases each type of basis function by one, and adds a new type of higher

Table 5.3 Composition in terms of contracted and primitive basis functions for the correlation consistent basis sets

Basis	Hydrogen		First row elements		Second row elements	
	Contracted	Primitive	Contracted	Primitive	Contracted	Primitive
cc-pVDZ	2s1p	4s	3s2p1d	9s4p	4s3p2d	12s8p
cc-pVTZ	3s2p1d	5s	4s3p2d1f	10s5p	5s4p3d1f	15s9p
cc-pVQZ	4s3p2d1f	6s	5s4p3d2f1g	12s6p	6s5p4d2f1g	16s11p
cc-pV5Z	5s4p3d2f1g	8s	6s5p4d3f2g1h	14s8p	7s6p5d3f2g1h	20s12p
cc-pV6Z	6s5p4d3f2g1h	10s	7s6p5d4f3g2h1i	16s10p	8s7p6d4f3g2h1i	21s14p

order polarization function. For second row systems it has been found that the performance is significantly improved by adding an extra tight *d*-function.[27]

The energy-optimized cc-basis sets can be augmented with diffuse functions, indicated by adding the prefix aug- to the acronym.[28] The augmentation consists of adding one extra function with a smaller exponent for each angular momentum, i.e. the aug-cc-pVDZ has additionally one *s*-, one *p*- and one *d*-function, the cc-pVTZ has 1s1p1d1f extra for non-hydrogens and so on. The cc-basis sets may also be augmented with additional *tight* functions (large exponents) if the interest is in recovering core–core and core–valence electron correlation, producing the acronyms cc-pCVXZ (X = D, T, Q, 5). The cc-pCVDZ has additionally one tight *s*- and one *p*-function, the cc-pCVTZ has 2s2p1d tight functions, the cc-pCVQZ has 3s3p2d1f and the cc-pCV5Z has 4s4p3d2f1g for non-hydrogens.[29]

5.4.7 Polarization consistent basis sets

The basis set convergence of electron correlation methods is inverse polynomial in the highest angular momentum functions included in the basis set, while the convergence of the independent-particle HF and DFT methods is exponential.[30] This difference in convergence properties suggests that the optimum basis sets for the two cases will also be different, especially should low angular momentum functions be more important for HF/DFT methods than for electron correlation methods as the basis set becomes large. Since DFT methods (Chapter 6) are rapidly becoming the preferred method for routine calculations, it is of interest to have basis sets that are optimized for DFT type calculations, and that are capable of systematically approaching the basis set limit. The *polarization consistent* (pc) basis sets are developed analogously to the correlation consistent basis sets except that they are optimized for DFT methods.[31] The name indicates that they are geared towards describing the polarization of the (atomic) electron density upon formation of a molecule, rather than describing the correlation energy. Since there is little difference between HF and DFT, and even less difference between different DFT functionals, these basis sets are suitable for independent-particle methods in general.

The polarization consistent basis sets again employ an energetic criterion for determining the importance of each type of basis function. The level of polarization beyond the isolated atom is indicated by a value after the acronym, i.e. a pc-0 basis set is

Table 5.4 Composition in terms of contracted and primitive basis functions for the polarization consistent basis sets

Basis	Hydrogen		First row elements		Second row elements	
	Contracted	Primitive	Contracted	Primitive	Contracted	Primitive
pc-0	2s	3s	3s2p	5s3p	4s3p	8s6p
pc-1	2s1p	4s	3s2p1d	7s4p	4s3p1d	11s8p
pc-2	3s2p1d	6s	4s3p2d1f	10s6p	5s4p2d1f	13s10p
pc-3	5s4p2d1f	9s	6s5p4d2f1g	14s9p	6s5p4d2f1g	17s13p
pc-4	7s6p3d2f1g	11s	8s7p6d3f2g1h	18s11p	7s6p6d3f2g1h	20s16p

unpolarized, pc-1 contains a single polarization function with one higher angular momentum, pc-2 contains polarization functions up to two beyond that required for the atom, etc. In contrast to the cc-pVxZ basis sets, the importance of the polarization functions must be determined at the molecular level, since the atomic energies only depend on s- and p-functions (at least for elements in the first two rows in the periodic table). For the DZ and TZ type basis sets (pc-1 and pc-2), the consistent polarization is the same as for the cc-pVxZ basis sets (1d and 2d1f), but at the QZ and 5Z levels (pc-3 and pc-4) there are one and two additional d-functions (4d2f1g and 6d3f2g1h), respectively. The s- and p-basis set exponents are optimized at the DFT level for the atoms, while the polarization exponents are selected as suitable average values from optimizations for a selection of molecules. The primitive functions are subsequently contracted by a general contraction scheme by using the atomic orbital coefficients.

For properties dependent on the wave function tail, such as electric moments and polarizabilities, the convergence towards the basis set limit can be improved by explicitly adding a set of diffuse functions, producing the acronym aug-pc-n.

5.4.8 Basis set extrapolation

The main advantage of the ANO, correlation consistent and polarization consistent basis sets is the ability to generate a sequence of basis sets that converges toward the basis set limit in a systematic fashion. For example, from a series of calculations with the 3-21G, 6-31G(d,p), 6-311G(2d,2p) and 6-311++G(3df,3pd) basis sets it may not be obvious whether the property of interest is "converged" with respect to further increases in the basis, and it is difficult to estimate what the basis set limit would be. This is partly due to the fact that different primitive GTOs are used in each of these segmented basis sets, and partly due to the lack of higher angular momentum functions. From the same (large) set of primitive GTOs, however, increasingly large ANO basis sets may be generated by a general contraction scheme that allows an estimate of the basis set limiting value. Similarly, the cc-pVxZ basis sets consistently reduce errors (both HF and correlation) for each step up in quality. In test cases it has been found that the cc-pVDZ basis can provide ~65% of the total (valence) correlation energy, the cc-pVTZ ~85%, cc-pVQZ ~93%, cc-pV5Z ~96% and cc-pV6Z ~98%, with similar reductions of the HF error.

Given the systematic nature of the cc basis sets, several different schemes have been proposed for extrapolation to the infinite basis set limit, using the highest angular momentum L_{max} included in the basis set as the extrapolating parameter.[32] At the HF and DFT levels the convergence is expected to be exponential, and indeed functions of the form shown in eq. (5.10) in connection with the cc-pVxZ basis sets usually provide a good fit.[33]

$$E(L_{max}) = E(\infty) + A e^{-BL_{max}}$$
$$E(L_{max}) = E(\infty) + A(L_{max} + 1)e^{-B\sqrt{L_{max}}}$$

$$(5.10)$$

An alternative fitting function (eq. (5.11)) for use with the pc-n basis sets has been shown to improve the accuracy of absolute energies by almost an order of magnitude, although relative energies are only marginally improved.[34] The number of s-functions (N_s) in the basis set is here used as the main extrapolating parameter.

$$E(L_{max}) = E(\infty) + A(L_{max} + 1)e^{-B\sqrt{N_s}}$$

$$(5.11)$$

Exponential forms like eq. (5.10) have also been used for extrapolating the total energy at correlated levels of theory with the cc-pVxZ basis sets. Theoretical analysis, however, suggest that the *correlation* energy itself (i.e. not the *total* energy, which includes the HF contribution) should converge with an inverse power dependence, with the leading term for singlet electron pairs being $(L + 1)^{-3}$ while the leading term for triplet pairs is $(L + 1)^{-5}$.[35] The theoretical assumption underlying these results is that the basis set is saturated in the radial part (e.g. a TZ type basis set should be *complete* in the s-, p-, d- and f-function space). This is not the case for the correlation consistent basis sets: even for the cc-pV6Z basis set, the errors due to insufficient numbers of s- to i-functions are comparable with that from neglect of functions with angular momentum higher than i-functions. Nevertheless, it has been found that extrapolations based on only the leading L^{-3} term give good results when compared with accurate results generated by for example R12 methods.[36] This has the advantage that the infinite basis set result can be estimated from only two calculations with basis sets having maximum angular momentum N and M according to eq. (5.12).

$$\Delta E_{corr,\infty} = \frac{N^3 \Delta E_{corr,N} - M^3 \Delta E_{corr,M}}{N^3 - M^3}$$

$$(5.12)$$

It has been suggested that a separate extrapolation of the singlet (opposite spin) and triplet (same spin) correlation energies with $A + B(L + 1/2)^{-3}$ and $A + B(L + 1/2)^{-5}$ function forms, respectively, may provide better results.[37]

The main difficulty in using the cc-pVxZ or pc-n basis sets is that each step up in quality roughly doubles the number of basis functions. The fitting functions in eqs (5.10) and (5.11) contain three parameters, and therefore require at least three calculations with increasingly larger basis sets. The simplest sequence is cc-pVDZ, cc-pVTZ and cc-pVQZ, but the cc-pVDZ basis is too small to give good extrapolated values for the correlation energy, and a better sequence is cc-pVTZ, cc-pVQZ and cc-pV5Z. The requirement of performing calculations with at least the cc-pVQZ basis places severe constraints on the size of the systems that can be treated. The extrapolation based on eq. (5.12) has the advantage of requiring only two reference calculations. It should be noted

that the *B* parameter in eq. (5.11) varies little from system to system, and taking this to be a universal constant also reduces eq. (5.11) to a two-parameter fitting function.

Perhaps the most interesting aspect of the analyses that led to the development of the correlation consistent basis sets is the fact that high angular momentum functions are necessary for achieving high accuracy. While *d*-polarization functions are sufficient for a DZ type basis, a TZ type should also include *f*-functions. Similarly, it is questionable to use a QZ type basis for the *sp*-functions without also including three *d*-, two *f*- and one *g*-function in order to systematically reduce the errors. It can therefore be argued that an extension of for example the 6-31G(d,p) to 6-311G(d,p) is inconsistent as the second set of d-orbitals (and second set of p-orbitals for hydrogen) and a set of *f*-functions (*d*-functions for hydrogen) will give similar contributions as the extra set of *sp*-functions. Similarly, the extension of the 6-311G(2df,2pd) basis to 6-311G(3df,3pd) may be considered inconsistent, as the third *d*-function is expected to be as important as the fourth valence set of *sp*-functions, the second set of *f*-functions and the first set of *g*-functions, all of which are neglected.

In the search for a basis set converged value, other approximations should be kept in mind. Basis sets with many high angular momentum functions are normally designed for recovering a large fraction of the correlation energy. In the majority of cases, only the electron correlation of the valence electrons is considered (frozen-core approximation), since the core orbitals usually are insensitive to the molecular environment. As the valence space approaches completeness in terms of basis functions, the error from the frozen-core approximation will at some point become comparable to the remaining valence error. From studies of small molecules, where good experimental data are available, it is suggested that the effect of core electron correlation for unproblematic systems is comparable with the change observed upon enlarging the cc-pV5Z basis, i.e. of a similar magnitude as the introduction of *h*-functions.[38] Improvements beyond the cc-pV6Z basis set have been argued to produce changes of similar magnitude to those expected from relativistic corrections for first row elements, and further increases to cc-pV7Z and cc-pV8Z type basis sets would be comparable with corrections due to breakdown of the Born–Oppenheimer approximation for systems with hydrogen. Within the non-relativistic realm, it would therefore appear that basis sets larger than cc-pV6Z would be of little use, except for extrapolating to the non-relativistic, clamped nuclei limit for testing purposes. In attempts at obtaining results of "spectroscopic accuracy" (~0.01 kJ/mol), a brute force calculation with for example the cc-pV7Z quality basis set combined with explicit extrapolation has been shown to become problematic,[37] and such high-quality results must probably be obtained by explicit correlated techniques, such as the R12 method discussed in Section 4.11.

There is a practical aspect of using large basis sets, especially those including diffuse functions, that requires special attention, namely the problem of *linear dependence*. Linear dependence means that one (or more) of the basis functions can be written as a linear combination of the other, i.e. the basis set is overcomplete. A diffuse function has a small exponent and consequently extends far away from the nucleus on which it is located. An equally diffuse function located on a nearby atom will therefore span almost the same space. A measure of the degree of linear dependence in a basis set can be obtained from the eigenvalues of the overlap matrix **S** (eq. (3.51)). A truly linearly dependent basis will have at least one eigenvalue of exactly zero, and the smallest eigenvalue of the **S** matrix is therefore an indication of how close the actual basis

set is to linear dependence. As described in Section 16.2.3, solution of the SCF equations requires orthogonalization of the basis by means of the $\mathbf{S}^{-1/2}$ matrix (or a related matrix that makes the basis orthogonal). If one of the $\mathbf{S}$ matrix eigenvalues is close to zero, this means that the $\mathbf{S}^{-1/2}$ matrix is essentially singular, which in turn will cause numerical problems if trying to carry out an actual calculation. In practice, there is therefore an upper limit on how close to completeness a basis set can be chosen to be, and this limit is determined by the finite precision with which the calculations are carried out. If the selected basis set turns out to be too close to linear dependence to be handled, the linear combinations of basis functions with low eigenvalues in the $\mathbf{S}$ matrix may be discarded.

5.5   Plane Wave Basis Functions

Rather than starting with basis functions aimed at modelling the atomic orbitals (STOs or GTOs), and forming linear combination of these to describe orbitals for the whole system, one may use functions aimed directly at the full system. For modelling extended (infinite) systems, for example a unit cell with periodic boundary conditions, this suggests the use of functions with an "infinite" range. The outer valence electrons in metals behave almost like free electrons, which leads to the idea of using solutions for the free electron as basis functions. The solutions to the Schrödinger equation for a free electron in one dimension can be written either in terms of complex exponentials or cosine and sine functions.

$$\phi(x) = A e^{ikx} + B e^{-ikx}$$
$$\phi(x) = A \cos(kx) + B \sin(kx) \tag{5.13}$$
$$E = \tfrac{1}{2} k^2$$

Note that the energy depends quadratically on the k factor. For infinite systems, the molecular orbitals coalesce into *bands*, since the energy spacing between distinct levels vanishes. The electrons in a band can be described by orbitals expanded in a basis set of *plane waves*, which in three dimensions can be written as a complex function.

$$\chi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \tag{5.14}$$

The wave vector $\mathbf{k}$ plays the same role as the exponent ζ in a GTO (eq. (5.2)), and is related to the energy by means of eq. (5.13) (conventionally given in units of eV). As seen in eq. (5.14), $\mathbf{k}$ can also be thought of as a frequency factor, with high $\mathbf{k}$ values indicating a rapid oscillation. The permissible $\mathbf{k}$ values are given by the unit cell translational vector $\mathbf{t}$, i.e. $\mathbf{k} \cdot \mathbf{t} = 2\pi m$, with m being a positive integer. This leads to a typical spacing between $\mathbf{k}$ vectors of ~0.01 eV, and the size of the basis set is thus uniquely characterized by the highest energy $\mathbf{k}$ vector included. A typical energy cutoff of 200 eV thus corresponds to a basis set with ~20 000 functions, i.e. plane wave basis sets tend to be significantly larger than typical Gaussian basis sets. Note, however, that the size of a plane wave basis set depends only on the size of the periodic cell, not on the actual system described within the cell. This is in contrast to the linear increase with