The Wavefunction

- All matter has both a wave and a particle like character, the De-Broglie relationship $\lambda = \hbar / \hat{p}$ tells us that anything that has momentum also has a wavelength.
- We should therefore be writing our molecular wavefunction in terms of a description of electrons *and nuclei* as waves.
- However, this is too complex, and we assume that the nuclear and electronic components can be seperated and that there is no coupling between them, ie not terms of the form: $\langle \Psi_{nuclear} | H | \Psi_{electronic} \rangle$
- The next assumption we make is that the molecular wavefunction can be written as a *simple product* of our electronic and nuclear waves, this is the Born-Oppenheimer approximation.
- This may seem trivial to you, but there is a whole, and very active, branch of theoretical chemistry which studies situations where this approximation breaks down, and this is not as rare as you might think!
- Next we make a second standard approximation, the nuclei are assumed fixed relative to the electrons, ie the kinetic energy of the nuclei is assumed to be zero ($T_N = 0$), this is the "*fixed nuclear approximation*" and is often conflated with the BO approximation.
- This is not unreasonable as the nuclei are are massive classical particles compared to the electrons and hence the electrons see nuclei that are essentially fixed in position
- The nuclear-nuclear interaction is now going to be a constant for any given configuration of the unmoving nuclei and we will ignore it from now on (it is actually added after solving the electronic Schrödinger equation).
- The nuclei, however, still effect the electrons through the electron-nuclear coupling potential.

$$H_e \Psi_e = E_e \Psi_e \quad \text{where} \quad H_e = T_e + V_{ne} + V_{ee}$$

- Quantum chemical methods are about solving the (time independent) *electronic* Schrödinger equation. The main effort goes into producing more and more sophisticated descriptions for the electronic wavefunction, Ψ.

Hydrogenic Orbitals

- We have a fundamental problem! We don't know what the orbitals for atoms with more than one electron look like, we cannot solve the equations! We assume they look like orbitals for the one system we can solve, the Hydrogen atom. Solving the electronic Schrödinger equation analytically for the Hydrogen atom gives us an analytic expression for single electron orbitals.
- "Analytic" means we can write a formula for something (ie f(x)=). "Numeric" means that we don't have a functional form for the relationship, (that could mean it doesn't exist, or that we don't want to go to the trouble of working it out). When we solve something numerically

we take values of x eg x=1, x=2, x=3 …etc and work out what f(1), f(2), f(3) is without knowing the general formula for f(x).

- Early in solving the Schrödinger equation for the Hydrogen atom we transform to spherical polar coordinates and assume that the wavefunction can be split into a radial (ie dependent on r) and an angular component (ie dependent on θ,ϕ).

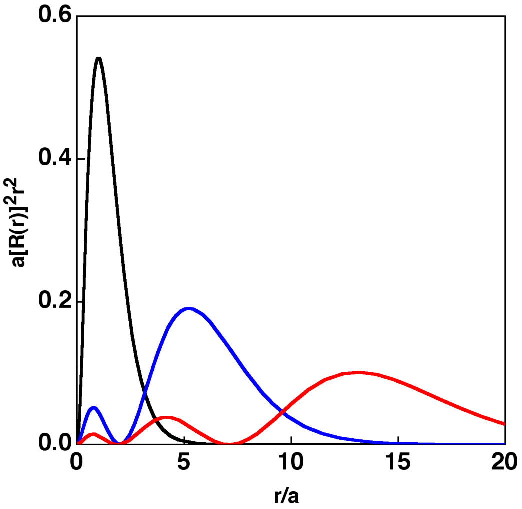


Figure 1 Radial distribution functions for 1s,2s,3s atomic orbitals

- The radial part gives us information on how far from the nucleus the electron likes to be (and is associated with the n quantum number, **Figure 1**)
- The angular part tells us if the electron likes to localise in particular regions around the nucleus, and is associated with the l and m_l quantum numbers which tell us the "shape" of the orbitals in space eg: s, p, d, f.
- Thus in setting up our equations for an atom or molecule, we cannot say what the final orbitals will look like, but we can assume that they will look like perturbed one-electron orbitals from the Hydrogen atom.
- This approximation is surprisingly good for the atomic orbitals, but we find that it is quite poor for molecular orbitals. However, we can improve our description of the molecular orbitals by adding more Hydrogenic type orbitals than we have electrons. Now we are using the Hydrogenic orbitals as a "*basis set*" to build up a description of the molecular orbitals.

What are Basis Sets?

- Basis functions are mathematical entities that we use to describe a function in space. I think showing you a simple example is the best way to get started.
- Consider a quite complicated geometric shape (equivalent of our final wavefunction), and a basis set of circles (related to our atomic basis set).
- **Figure 2(a)** is the shape I want to describe (a car), and **Figure 2(b)** shows how well I could describe this shape with a single basis shape (a circle). I use circles because they are easy to compute and hence reduce the cost of a calculation.

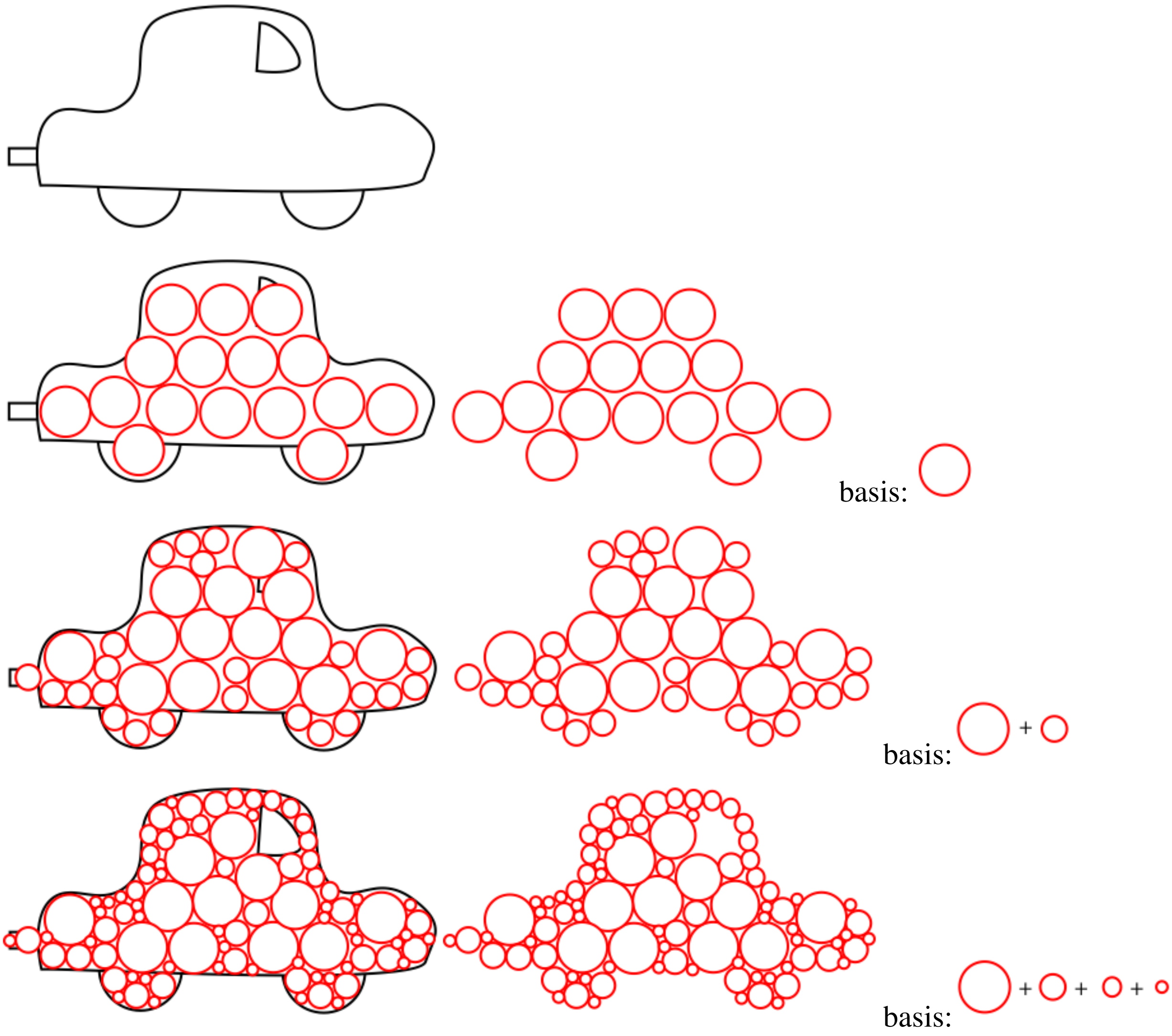


Figure 2 Basis-Fuctions

- **Figure 2(c)** shows how well I could do if I allowed my circles to vary slightly in size, my basis now consists of two functions, and **Figure 2(d)** shows an even better fit if I add more functions to my basis set.
- Notice also how the complexity and detail of the car gets better as I use more functions. If I label each circle as a function f_i, then my car shape can be described as a sum of circles (functions) the centers of which are determined by some coordinates (x,y) and the size of which can be varied by the coefficient C_i.

$$car = \sum_i C_i f_i(x,y)$$

- A basis set is thus a mathematical way of describing a complicated function using simpler functions. There are rules governing how these functions come together, for example they must remain independent (the analogy would be that circles cannot overlap) and they must "span the space" of the original function (the analogy would be that the circles must be able to fill the space covered by the car). To exactly describe a real function will actually take an infinite number of basis functions however in general a very good approximation can be made with fewer functions (the analogy here would be to exactly reproduce the car with no gaps and no overlapping).

- Another way of thinking of basis functions (quite different from the above) is as a coordinate space, the unit vectors of which are the basis functions. For example, we can describe a Cartesian vector as $\hat{r} = x\hat{i} + y\hat{j} + z\hat{k}$, where i, j, and k are the usual unit vectors or basis vectors, or basis functions for the Cartesian space. If $\hat{r}$ had a component outside of Cartesian space, the Cartesian vectors would not be enough to describe it. In this case the basis vectors would not span the space of the function ($\hat{r}$). Thus our basis functions (atomic orbitals, AOs) describe a space, and a linear combination of these functions, defines a more complex function (the molecular orbital, MO) within this space.

$$MO = c_1 AO_1 + c_2 AO_2 + \cdots + c_n AO_n = \sum_{i=1,n} c_i AO_i$$

- We call it a *linear combination* because none of the functions is raised to a power greater than 1. The basis above has a dimension, n where n is the number of basis functions. The coefficients in the above equation are determined during a calculation. We optimise them so that the energy of our molecule is at a minimum (this is how we tell we have a good set of coefficients). For the more technically minded; we require $\partial E / \partial c_i = 0$ for all c_i.

Orbital Basis Functions

- We could use the atomic orbitals from the solution of the Schrödinger equation for the Hydrogen atom as a basis to describe the orbitals of a molecule:

Z=atomic charge on the nucleus, and $a = 4\pi\varepsilon_0 \hbar^2 / m_e e^2 = 0.5292\mathring{A}$.

$$R_{1s} = 2\left(\frac{Z}{a}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a}}$$

$$R_{2s} = \frac{1}{\sqrt{2}}\left(\frac{Z}{a}\right)^{\frac{3}{2}}\left(1 - \frac{Zr}{2a}\right) e^{-\frac{Zr}{2a}} \qquad R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a}}$$

$$R_{3s} = \frac{1}{3\sqrt{3}}\left(\frac{Z}{a}\right)^{\frac{3}{2}}\left(1 - \frac{2Zr}{3a} + \frac{2Z^2r^2}{27a^3}\right) e^{-\frac{Zr}{3a}} \qquad R_{3p} = \frac{8}{27\sqrt{6}}\left(\frac{Z}{a}\right)^{\frac{3}{2}}\left(\frac{Zr}{a} - \frac{Z^2r^2}{6a^2}\right) e^{-\frac{Zr}{3a}}$$

$$R_{3d} = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a}}$$

- If you look at the radial component of the Hydrogen orbitals you will see that they have a common exponential factor $\psi \propto e^{-Zr/a}$ that is modified by a special type of polynomial (called an *Associated Laguerre function*). The angular part are just *Sperical Harmonic functions* $Y(\theta,\phi)$

AO=> $N\left(polynomial\ in\ r^{(n-1)}\right) e^{-\zeta r/a} Y(\theta,\phi)$

- However we don't use exactly these same orbitals because the polynomials are too complex (we keep the spherical harmonics because they are relatively simple).
- The orbitals we actually use are called "Slater Type Orbitals" (or STO's for short, remember this acronym, as it is used frequently). Slater Type Orbitals resemble atomic orbitals closely.

$$\text{STO=>}\, Nr^{(n-1)}e^{-\zeta r/a}Y(\theta,\phi)$$

- However, as even STO can be difficult to deal with mathematically, another type of basis function is often used, these are "Gaussian type orbitals" (or GTOs).

$$\text{GTO=>}\, Nr^{l}e^{-\zeta r^2}Y(\theta,\phi)$$

- N=normalisation factor, this allows functions to be compared on the same footing. ζ is not same for each orbital type (I've just used it to simplify the expressions).

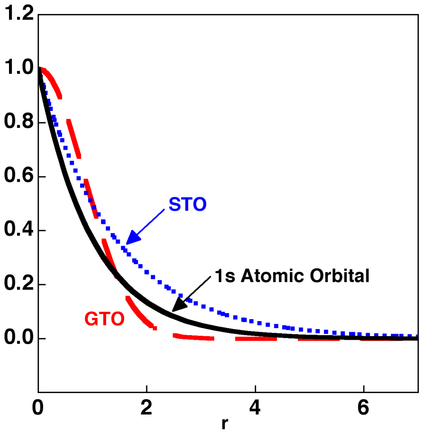


Figure 3 Comparison of a s-type Atomic Orbital, STO and GTO

- Slater type orbitals have the correct functional behaviour near the nucleus, ie a cusp and decay in the correct way at long distances (**Figure 3**). Gaussian type orbitals provide a relatively poor description of the atomic orbitals, they have a finite value at the nucleus and decay too quickly (thus underestimating long range interactions).
- The incorrect decay of the gaussian is due to the gaussian having an exponential in r^2 while the STO has an exponential in r. Typically it will take 3 or more gaussians to describe one atomic orbital, but they are very efficient. In calculations the time taken to evaluate 3 GTOs is actually less than the time it takes to evaluate one STO!
- Thus, in general, GTOs cannot describe well electron density near the core, or well away from the atom. This means that properties which depend on electron density near the core (like NMR), or far away from the atom (such as in negatively charged species, or in H-bonding) have to be treated vary carefully.
- However, the STOs are not perfect either, note that the polynomial in r has been replaced by a single power of r, thus the STO does not have the proper number of radial nodes and does not well represent the inner part of an orbital.

- In both cases there is no loss in accuracy as long as *enough* of these new functions are used such that there is an adequate description of the final molecular orbitals. We use one or the other of these functions as basis functions, we never mix basis function types.

Gaussians

- Most quantum chemical codes use Gaussians for basis sets, so to understand the designation of a basis set you need to understand something about Gaussian functions. Gaussian is the general name given to functions of the form: $e^{-\zeta(r-r_0)^2}$ (where ζ (Greek zeta) is the exponential coefficient). ζ determines the spread of a gaussian function, for example, a large value of ζ gives a tight gaussian and ζ small value of a gives a diffuse gaussian, **Figure 4**. The position of a gaussian is determined by r_0, and is normally an atomic center. The height of the gaussian will be determined by a preceding coefficient.

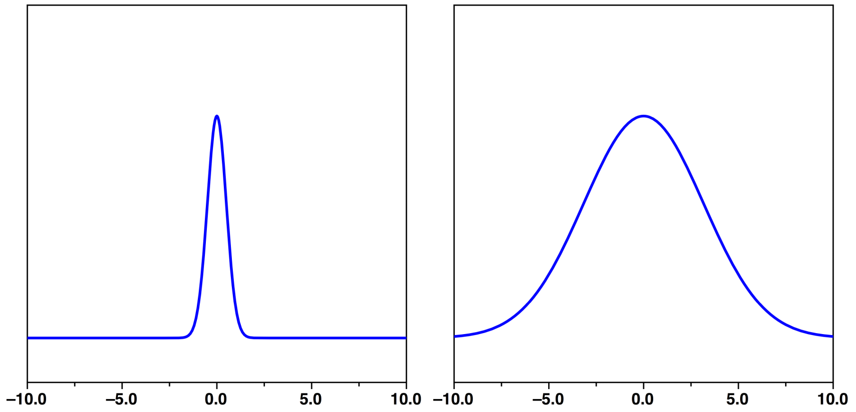


Figure 4: (a) $g(x)=e^{-2.0(x)^2}$ and (b) $g(x)=e^{-0.05(x)^2}$

- Gaussians are very useful and computationally efficient because the product of any two gaussians is just another gaussian**, Figure 5(a)**, and the sum of two gaussians is easily evaluated, **Figure 5(b)**.

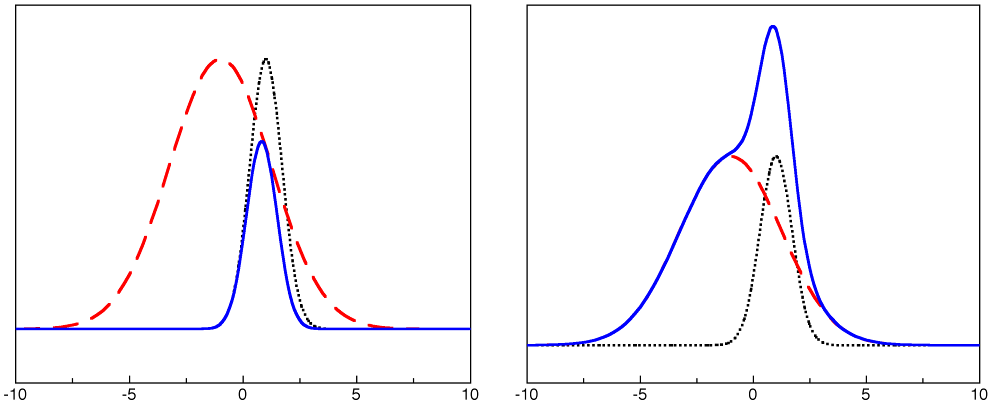


Figure 5 (a) solid: $g_3(x)=g_1(x)*g_2(x)$, (b) solid: $f(x)=g_1(x)+g_2(x)$, where the dotted function $g_1(x)=e^{-0.1(x+1)^2}$ and dashed function $g_2(x)=e^{-1.0(x-1)^2}$

- This property is very important in quantum chemistry because we have to evaluate integrals of the form given below. The first is called a "4 center" integral and is easily reduced to a "2 center integral" when using gaussians.

$$\int g_1 g_2 \frac{1}{r_{12}} g_3 g_4 \, d\tau = \int g_a \frac{1}{r_{12}} g_b \, d\tau$$

Minimal Basis Set

- The STO *coefficients* and *exponents* are fit to a numerically determined ie "real" atomic orbital. Thus as the 1s AO of carbon differs from the 1s AO of oxygen, so the STO for each of these 1s AOs will differ.
- A "minimum basis set" uses 1 STO to describe each atomic orbital in the ground state of an atom. For shells with more than one angular component this means one function for each angular component. For example we need three 2p STO for the 2p valence shell because the electron spends 1/3 of its time in each 2p orbital (eg $2p_x$, $2p_y$, $2p_z$).
- For example:

H	$1s^1$	one 1s STO
Li	$1s^2 2s^1$	one 1s STO + one 2s STO
C-F	$1s^2 2s^2 2p^n$	one 1s STO + one 2s STO + three 2p STOs

- A minimal basis set is just that, minimal, they have significant deficiencies.
- For example, all the atoms in a row will have the same basis set (see C, N, O above). They may have the same form of basis set, but for each atom the coefficients and exponents will be different. This means that the atoms at the beginning of a row will have a *better description per electron* than those at the end.
- The radius of each orbital is set so the orbitals *cannot expand or contract* to adjust to the molecular environment. For example if we added an electron to form a negative ion, the radial extent of the orbitals could not change. Also as you move along the row more electrons are added into the same "space", this increases electron-electron repulsions which may otherwise have been alleviated by a slight expansion in the orbitals.
- The *shape of each orbital is set*, and cannot respond to any local anisotropy (ie an unsymmetrical environment). For example in HF the hydrogen 1s electron is attracted toward the F atom, but it cannot move because the 1s orbital is spherical.
- We never make a Gaussian minimal basis set as the gaussians make too poor an approximation to the real atomic orbitals. However, there is one type of basis set called a STO-nG basis. It starts with a minimal STO basis (ie with one STO describing each atomic orbital), the STO exponents are *optimised* for the atomic orbital, and then each STO is modelled by a linear combination of n-Gaussians, where the coefficients and exponents of the Gaussians are *fitted* to the STO.

Note that I have used "fit" rather than "optimised" when talking about the procedure for determining the coefficients of the gaussians. For these basis sets, the STO are optimised, ie their coefficients and exponents are found by *minimising the energy* in an atomic calculation, they are then fixed. The gaussian coefficients and exponents are found by *determining the least error* when comparing the two functional forms.

- For example, if we use 3 gaussians to model each STO of our minimum basis set, then the basis set is called the "STO-3G" basis set, **Figure 6**.

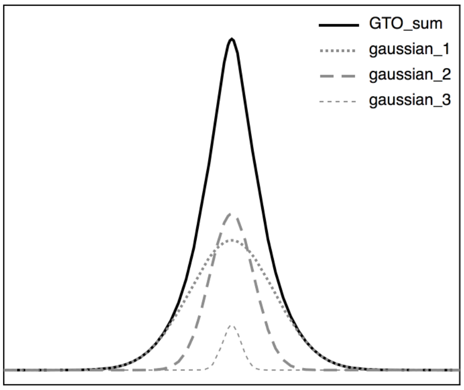


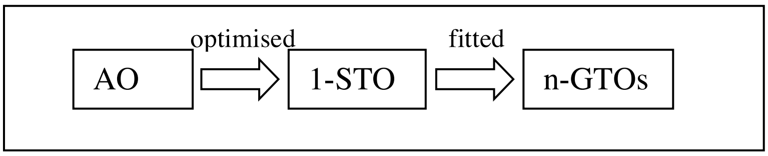
Figure 6: Sum of three 1s gaussians for oxygen

- consider one orbital on an atom in a molecule:

$$d_1\left[STO\right] = d_1\left[c_1 g(\alpha_1) + c_2 g(\alpha_2) + c_3 g(\alpha_3)\right]$$

  - the exponents inside the STO have been pre-optimised to an atomic system (ie if we used this atom in a different molecule these would remain the same)
  - the GTO coefficients c_i and exponents α_i (i=1,3) are fixed (fitted to the atomic STO)
  - d_1 is the only variable which is optimised during a normal calculation
- There is an increasing hierarchy of basis sets of this type, that uses an increasing number of gaussians to describe each STO. In general the more gaussians we use to describe the STO the better the fit. (However, there does come a point where the gaussians become linearly dependent and then adding more functions is not useful).

possibilities are:
STO-3G
STO-4G
STO-6G



- Some real numbers are shown below for an STO-3G basis set.

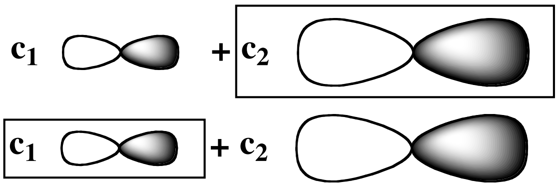
```
1S   3 1.00
     .1307093214E+03   .1543289673E+00
     .2380886605E+02   .5353281423E+00
     .6443608313E+01   .4446345422E+00
2S    3 1.00
     .5033151319E+01  -.9996722919E-01
     .1169596125E+01   .3995128261E+00
     .3803889600E+00   .7001154689E+00
2P   3 1.00
     .5033151319E+01   .1559162750E+00
     .1169596125E+01    .6076837186E+00
     .3803889600E+00    .3919573931E+00
```

the first set of numbers describe the 1s AO
lets look at the first line: S 3 1.00
S=s orbital
3=number gaussians
1=coefficient for the whole orbital
then lines 2,3,4 list the exponent first (ie ζ_1) and the coefficient second (ie c_1).

- Remember we have taken an atomic orbital (real orbital), then found the *best* Slater type orbital that resembles it, but the STOs (complex function) are too difficult to use in calculations so we *fit* Gaussian type functions (simple function) to the STO for computational ease. We then vary a coefficient to the STO which determines its contribution to a MO (the coefficients to the GTO "inside" the STO remain fixed).
- Producing basis sets may sound simple, but there are complexities and details (which we will not be discussing) which mean this procedure is not trivial. There are people who spend most of their research lives producing very good basis sets for the rest of us to use.
- Not all atoms have basis sets! Especially for heavy atoms a basis set may not exist.

n-Zeta Basis Sets

- We can improve the situation by using more than one STO or more than one GTO to describe each atomic orbital, this allows the basis set to better represent the real electron density. I'm going to just refer to STOs in the following but the same applies for GTOs.
- For example, if we have a negative ion, and we have only a single frozen orbital the mutually repulsive electrons cannot move away from each other, however if we have a basis set that has a component with a small exponent (leading to a diffuse orbital) and a larger exponent, then the electrons can "move" into the more diffuse orbital, by increasing the coefficient for the diffuse orbital.



negative ion c_1 small c_2 large

positive ion c_1 large c_2 small

- A *double zeta* (DZ) basis set has 2 STOs for each AO, a *triple zeta* (TZ) basis set has 3 STOs and a *quadruple zeta* (QZ) basis set has 4 STOs per AO, and so on. Why do we say "n-zeta" basis set? This is because the exponent (ζ_n) is the Greek letter "zeta". For example, a *single* atomic orbital in a TZ STO basis will be described as below where each s_i varies as the calculation proceeds:

$$AO = s_1 STO(\zeta_1) + s_2 STO(\zeta_2) + s_3 STO(\zeta_3)$$

- In order to quickly see how many functions are used for a particular atom in a calculation a short hand notation has been developed to indicate the number of functions. The total number of s, p, d etc *sets* of functions is specified within round brackets. (Don't forget for all the pAOs we need a set of 3STOs one for each of the p_x, p_y and p_z AOs) For example:

H	$1s^1$	DZ	(2s)
		TZ	(3s)
C	$1s^2 2s^2 2p^2$	DZ	(4s2p)
		(eg 2 (1s)STOs + 2 (2s)STOs + 2sets of 2pSTOs)	
		TZ	(6s3p)

- In general all the atoms in a molecule should have the same kind of basis set and so the shorthand notation is given only once. However, Hydrogen is often a special case and its basis set is given after the heavier elements. For example, for the first row elements:

DZ basis	(4s2p,2s)
TZ basis	(6s3p,3s)

- There are also cases where the 3d TM or 4f Actinides and Lanthanides are treated slightly differently from atoms in the first and second row of the periodic table, in this case additional designators can be given (3rd row, 1st and 2nd row, H)

Valence n-Zeta, Contracted and Split-Valence Basis Sets

- Increasing the number of STOs increases the computational cost substantially. We can be smarter about how we improve our orbital description.
- We can split our basis set into a core and a valence component, core orbitals are described by a single STO, while the chemically important valence orbitals are described by more STOs. Over time this approximation (as it relates to basis sets) has been proven to be an extremely good one. When this approximation is used we say the basis is a "*Valence n-Zeta*" basis set, eg VDZ (valence double-zeta), VTZ (valence triple-zeta), VQZ (valence quadruple-zeta) and so on.
- For example:

C $1s^2 2s^2 2p^2$ (3s2p,2s) VDZ basis
(eg 1 (1s)STO for the core + 2 (2s)STOs + 2sets of 2pSTOs, and 2 (1s)STOs for the hydrogen atoms)

- However, while the core density does not move like the valence density, describing it well is very important in terms of the total energy. Most of the "energy" comes from electrons near the nucleus, they experience the largest forces (potentials) and they go faster, have more kinetic energy. To obtain the best energies you must have a good description of the core electrons. It makes sense therefor to expand the core STOs using a much larger set of STOs than we do the valence STOs.
- When we do this we start with "*primitive*" guassian functions, which we "*contract*" in a specific pattern. Overall the basis set is less flexible once contracted, but the reduction in the computational cost is significant especially for large basis sets. The use of contracted basis sets is almost ubiquitous in computational chemistry today.

for example 3 primative gaussians are completely contracted into one STO:

$$STO_{core} = \underbrace{d}_{\text{var}\,iable} \{c_1 g(\alpha_1) + c_2 g(\alpha_2) + c_3 g(\alpha_3)\}$$

- It has also been found that the inner part of the valence orbitals can be contracted (ie frozen). When this is done, the valence basis set is said to be "*split*".

for example 3 primative gaussians are contracted in a pattern of 2:1 into one STO:

$$STO_{valence} = \underbrace{d_1}_{\text{var}\,iable} \{c_1 g(\alpha_1) + c_2 g(\alpha_2)\} + \underbrace{d_2}_{\text{var}\,iable} \{c_3 g(\alpha_3)\}$$

- The type of contraction is also indicated using the shorthand notation, first the primitive basis set is given in round brackets, and the contraction in square brackets.

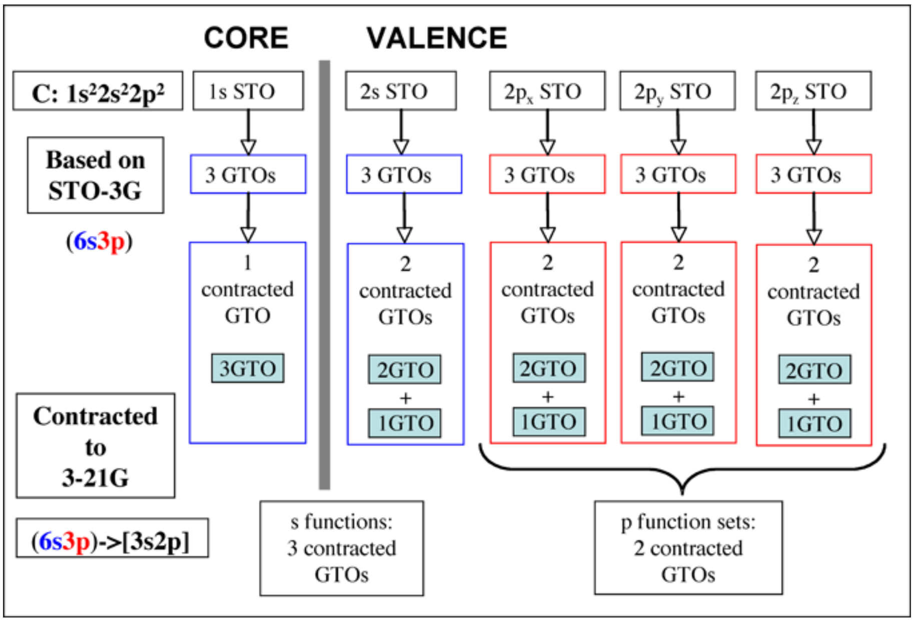
  the basis in the examples above is 3-21G described as a (6s3p,3s)->[3s2p,2s] and is not quite a full VDZ gaussian basis because of the core description

Types of Basis Sets

- Just as media companies can't agree on a standard format for music, or even text files, quantum chemists cannot agree about basis sets. Part of the problem is that basis sets are (and must be) specific to the system and properties to be studied.
- There are two main types of basis set that are most commonly used, these are the basis sets developed by Pople and co workers and those developed by Huzinaga & Dunning. Of these contracted double and triple zeta split valence basis sets are very common. Of course there are other varieties out there, these two are just the most common.
- These basis sets have been used for some time now and are well tested, their accuracy (good) is well established. In general, the Pople basis sets are considered less accurate than the Huzinaga and Dunning sets, but as the Pople basis sets were developed first and are widely incorporated into many key quantum chemical packages, they have a wider user base.
- John Pople received the Nobel Prize in Chemistry in 1998 for work in part that included the development of these types of basis sets. Pople basis sets are good basis sets for "inexperienced" users, Huzinaga & Dunning basis sets are important if you want a highly accurate result.

Pople Basis Sets

- Pople basis sets are based on the STO-nG minimal basis sets where n-contracted gaussians are used for each core orbital and a less contracted set are used for the valence orbitals. These basis sets are sometimes called VDZ (or VTZ) but in fact are not quite of this quality because they are based on a minimal description of the core orbitals. In addition the s and p orbitals of the same shell have the same exponents, and same contraction pattern.
- You have already met the 3-21G contracted basis set. In this basis 3 contracted primitive gaussian functions are used for the core and 3 primitive gaussian functions contracted in the pattern of 2 and 1 are used for the valence orbitals.



- The 4-31G basis is also derived from the STO-4G basis. (Note that the final contraction is the same as that for the 3-21G basis, but this basis is slightly better because more GTOs have been used.)

4-31G (second row element $1s^22s^22p^2$)
core 1s => 1 STO in terms of 4 GTO contracted into 1 GTO
valence 2s => 1 STO in terms of 4 GTO contracted into 2 GTO in a 3:1 pattern
valence 2p => 1 set of STOs each in terms of 4 GTO contracted into 2 in a 3:1 pattern
designation (8s4p,4s)->[3s2p,2s] (not quite a VDZ gaussian basis)

- The 6-31G basis is slightly different again.

6-31G
core 1s => 1 STO in terms of 6 GTO contracted into 1 GTO
valence 2s => 1 STO in terms of 4 GTO contracted into 2 in a 3:1 pattern
valence 2p => 1 set of STOs each in terms of 4 GTO contracted into 2 in a 3:1 pattern
designation (10s4p,4s)->[3s2p,2s] (not quite a VDZ gaussian basis)

- The 6-311G basis is also slightly different.

6-311G
core 1s=> 1 STO in terms of 6 contracted GTOs contracted into 1 GTO
valence 2s => 1 STO in terms of 5GTO contracted into 3 in a 3:1:1 pattern
valence 2p => 1 set of STOs each in terms of 5GTO contracted into 3 in a 3:1:1 pattern
designation (11s5p,5s)->[4s3p,3s] (not quite a VTZ gaussian basis)

- A rough list of the ordering of these basis sets is STO-3G < 3-21G < 4-31G < 6-31G < 6-311G
- The STO-3G basis set is used for rough calculations, and seldom appears in published work. The 3-21G, 4-31G basis sets are low level and are often used to make a first guess at geometries before shifting to a higher basis set to finish optimising a structure. These basis sets are sometimes used in systems where a core set of atoms is being described well, and the outer part less well (peripheral groups), these basis sets are used on the outer part. If you are looking at a calculation that has used one of the

"lesser" basis sets, you should realise that there may be substantial errors.

- The 6-31G, 6-311G basis sets (and some related to them which we will talk about later) are the work-horse basis sets for many computational studies and are a basic standard in published work.
- Pople basis sets exist for H and the first row of the periodic table and for most of the second row and transition metal elements, there are few Pople basis sets for higher level atoms. This is because these basis sets were originally designed to treat first and second row atoms and organic molecules, they are not parameterised for heavy atoms, and do not have high angular momentum functions (f,g,h) which are required to treat heavy atoms properly.
- Warning! In programs like Gaussian you may give a keyword to call a specific basis set, however, you may not get exactly the basis set specified by this "name". What you are getting is a basis set of roughly this quality. You should always go to the package manual and to any references supplied with the basis set to ascertain exactly the form of the functions used.
- For example in Gaussian calling the such as 6-311G: "Specifies the 6-311G basis for first-row atoms and the McLean-Chandler (12s,9p) → (621111, 52111) basis sets for second-row atoms (note that the basis sets for P, S, and Cl are those called negative ion basis sets by McLean and Chandler; these were deemed to give better results for neutral molecules as well), the basis set of Blaudeau and coworkers for Ca and K, the Wachters-Hay all electron basis set for the first transition row, using the scaling factors of Raghavachari and Trucks, and the 6-311G basis set of McGrath, Curtiss and coworkers for the other elements in the third row."
- For example calling the 6-311G basis set for Ca returns:

```
Ca    0
S   6   1.00                                       P   3   1.00
 202699.0000000        0.000222964                  1019.7600000       0.00205986
  30382.5000000        0.00172932                    241.5960000       0.01665010
   6915.0800000        0.00900226                     77.6370000       0.07776460
   1959.0200000        0.0366699                   P   3   1.00
    640.9360000        0.1194100                      29.1154000       0.2418060
    233.9770000        0.2918250                      11.7626000       0.4325780
S   2   1.00                                           4.9228900       0.3673250
     92.2892000        0.4044150                   P   1   1.00
     37.2545000        0.2963130                       1.9064500       1.0000000
S   1   1.00                                       P   1   1.00
      9.1319800        1.0000000                       0.7369000       1.0000000
S   1   1.00                                       P   1   1.00
      3.8177900        1.0000000                       0.2764200       1.0000000
S   1   1.00                                       P   1   1.00
      1.0493500        1.0000000                       0.0602700       1.0000000
S   1   1.00                                       P   1   1.00
      0.4286600        1.0000000                       0.0179100       1.0000000
S   1   1.00                                       D   3   1.00
      0.0628226        1.0000000                      15.0800000       0.0368947
S   1   1.00                                           3.9260000       0.1778200
      0.0260162        1.0000000                       1.2330000       0.4255130
```

Dunning-Huzinaga and Correlation Consistent Basis Sets

- Huzinaga basis sets are obtained by carrying out atomic high level calculations using very large uncontracted basis sets and then contracting them. These basis sets are not split-valence, but fully double, triple, quadruple etc valence. These basis sets are normally referred to by the basic acronyms VDZ, VTZ, VQZ etc and then the specific contraction in the form (spd)->[spd]. The contraction pattern may or may not be specified, but is understood and can be obtained from the original papers in which the basis sets were first published. For example:

DZ		TZ	
H	(4s)->[2s]	H	(5s)->[3s]
first row	(9s5p)->[4s2p]	first row	(10s5p)->[5s3p]
contraction	6,1,1,1 and 4,1	contraction	5,3,1,1,1 and 4,1,1

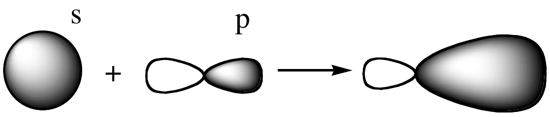
- Dunning has produced some "*correlation consistent*" basis sets based on the Huzinaga development for use with methods that recover electron correlation. These basis sets are specified by adding "*cc*" to the Huzinaga specifications. The basic basis sets are gradually improved by adding sets of core (s and p) and then higher angular momentum functions. Unlike the Pople basis sets, there is a systematic addition of functions. The larger sets are *very* expensive and consist of 30 or 55 basis functions *per atom* (for second row), however they recover a well defined amount of valence-correlation.

cc-pVDZ: (9s4p) + 1s1p1d	-> [3s2p1d]	14 functions
cc-pVTZ: (10s5p) + 2s2p2d1f	-> [4s3p2d1f]	30 functions
cc-pVQZ: (12s6p) + 3s3p3d2f1g	-> [5s4p3d2f1g]	55 functions

cc-pVDZ (recovers 65%)
cc-pVTZ (recovers 85%)
cc-pVQZ (recovers 93%)

Polarization Functions

- We have improved our description of the valence electrons, in the valence n-zeta basis sets. This has introduced radial variation in the symmetry of the electron density around an atom. We have compensated for the additional computational cost of moving to n-zeta by contracting the core description.
- We now need to deal with the polarization of electron density in a non-spherical manner, ie in a specific direction as occurs in a polar bond. We do this by introducing "*polarization*" functions. These are just functions of a higher angular momentum than the valence shell. For example, mixing some pAO character into an sAO allows it to polarize, and the electron density can distort to one side of an atomic nucleus:



HOMO orbital	polarisation function
s	p,d,f
p	d,f
d	f,g

- Polarisation functions also play other important roles. In any system where the electron density can be expected to be polarized (ie will move depending on the local environment) polarization functions are required, this can be systems where the e-density is easily polarized (eg soft atoms), or systems with strongly charged local environment (eg highly polar systems), or systems with an external potential (in an electric field). Examples include systems with large dipole moments, atoms with a significant polarizability (eg S), anions with large diffuse electron clouds (eg I-), compounds with very electronegative or electropositive atoms, and molecules exposed to strong electric fields (electrochemical or light driven reactions).
- Polarisation functions are always added as sets, ie a set of 3p functions, 5d functions, 7f functions. For Pople basis sets "*" indicates the addition of polarisation functions, eg 6-31G*, after the first set of polarization functions has been added they are then identified explicitly for each atom, and the exponents identified. For Huzinaga basis sets polarization functions are indicated by adding P on the end of the acronym.

6-31G(d)=6-31G*, 6-31G(2d), 6-31G(2df), 6-31G(3df).
DZP, VTZ2P, VQZ3P

- Polarisation functions should not be added to a poor basis set, the rule of thumb is to have one less n-zeta than you have polarisation functions. Thus adding two sets of d-functions (one with smaller and one with larger exponents) to 6-31G basis set should not really be contemplated, unless you have a very good reason, and some knowledge of the errors or artefacts that may creep into your calculations.
- For systems with large correlation effects large basis sets that include polarization functions are required, a TZ2P basis set is considered a "minimum" (if it can be managed!) for getting reasonable results. In many organo-metallic and large inorganic calculations a basis set of this size often requires the use of a model compound to reduce the number of electrons.
- There is a limit to the functions programs are set up for, normally f but sometimes g. Heavy elements generally have to be treated by "special" basis sets, and often the basis set is stated explicitly. For example a 6-31G basis sets are only defined up to Kr and only a maximum of (3df,3pd) can be added in the program Gaussian. Other programs will have other limits.

Diffuse Functions

- Diffuse functions allow us to describe electron density that has spilled out from the main occupied orbitals. These are (s, p and d) functions with a small exponent, and they help to improve the description of the electron density away from the core (remember that Gaussians have the wrong long range decay, so adding extra functions in this region goes to improving this).
- Systems which benefit from diffuse functions include atoms with lone pairs (eg N, P, As …), large polarizable atoms (eg I), negatively charged species, systems with low lying excited states (3d TMs) and atoms with low lying unoccupied orbitals (eg Si, P).
- Augmented basis sets are good for describing weakly bound complexes, eg Van der Waals, Hydrogen bonding, proton affinities, transition state barrier heights and strongly polar species.
- If we want to describe properties that depend on the electron density far from the nucleus we will need diffuse functions (eg dipole moments). If higher order properties are required (those that relate to a 2nd or higher derivative of the energy, such as the polarizability) then more diffuse functions are required.
- If Pople basis sets are being used a "+" is used before the G for the first set of functions, eg 6-31+G, after this any more diffuse functions are given explicitly for each atom along with their exponent. When using Huzinaga & Dunning basis sets, "*aug*" is prefixed to the basis set descriptor, for example: aug-cc-pVDZ, if more are required the basis set is doubly (d-aug-cc-pVDZ) or triply augmented (t-aug-cc-pVDZ).
- Diffuse functions come at a cost, they make optimisation unstable and add significantly to computing time, more so than other functions. There is no point in adding diffuse functions unless the valence and core description is already a good one. In general diffuse functions should not be added unless the base basis set is already double zeta (or almost double zeta in the case of Pople basis sets). Normally 2 sets of diffuse functions (1s and 3p) are sufficient, however three can be added, in which case the valence description should be at least triple zeta.

Hydrogen

- Hydrogen atoms need special consideration. There can be many of them in a complex, and adding extensive basis sets and additional functions can rapidly make a calculation too large to be performed. Where Hydrogen atoms are not active it is customary to use a reduced basis set, one of the simplest ways of doing this is leaving the polarization and diffuse functions off the Hydrogen atoms, as these functions are often most important for heavy atoms. Hence when specifying the basis set for a calculation the Hydrogen atom basis function are often given separately, after a comma: (spd,sp)/[spd,sp].
- For example a calculation performed using a 6-31+G basis set will add one set of diffuse functions (1s & 3p) to all the heavy atoms *only*. The 6-31++G basis set has one set of diffuse functions on the heavy atoms, and onto the Hydrogen atoms as well.
- The 6-31G*=6-31G(d) basis set adds one set of polarization functions (5d for 2nd row and 7f for the 3rd row) to all the heavy atoms. The 6-

31G**=6-31G(d,p) basis set adds one set of polarization functions to the heavy atoms and a set (3p) to all the Hydrogen atoms. 6-311G(2df,2pd) is a very large basis set and adds two sets of d functions and one set of f functions to each heavy atom (that's 24 extra functions per heavy atom!) and then 2 sets of p functions and one set of d functions per hydrogen (that's 16 extra functions per hydrogen atom!). This basis set could only be used for calculations on a relatively small system.

Balanced Basis Sets

- If you want to compare calculations, they must be carried out using the same method and with *exactly* the same basis set. This is because we do not use infinite basis sets, and there is a *substantial error in the absolute energies* that we calculate. However, since a large part of this error is systematic and eliminated when we compare two numbers we can evaluate *energy differences*.
- In reality this is quite problematic between research groups as everyone uses slightly different basis sets. Energies determined using different basis sets should never be directly compared. However, if you are interested in qualitative information, properties such as geometries, frequencies, and NMR, are less basis set dependent and can be compared for *similar* basis sets and methods.
- If your basis is poorly balanced one thing that can happen is that one atom can "steal" basis sets from a nearby atom to improve its own flexibility (especially if the other atom has diffuse functions). Atoms don't even have to be bonded, it could be an atom using unoccupied (virtual) basis functions from alkyl side-chains or bulky substutents.
- Even if your basis set is well balanced, this effect can be significant if you are comparing numbers of almost equal magnitude.
- When computing clusters it is possible for atoms in monomer one to "use" functions from monomer two. If each monomer is calculated in isolation then there is no problem, but when a weakly bound cluster is described this becomes and issue. Essentially you are using different basis sets for each calculation.
- This is a particular problem if you are trying to model weak bonding interactions such as van der Waals interactions, clusters or Hydrogen bonds. In weakly bound clusters there can be a shortenting of intermolecular distance and overbinding due to this problem.
- This error is called the "*Basis Set Superposition Error*" or BSSE. When the basis sets are "stolen" internally from the same molecule this is intramolecular BSSE, when the basis sets are "stolen" from another molecule this is intermolecular BSSE. The issue becomes more complex when considering transition states, are there one, two or three molecular components and how do you define them.
- An approximate way of assessing the BSSE is the "*Counterpoise (CP) correction*" of Boys and Bernardi (Mol. Phys, 1970, 19, p553). If the energy of the complex (or dimer or cluser etc.) ab is computed using basis sets A and B and the energy of the monomer computed using basis set A, and the energy of the monomer computed using basis set B, to determine the association energy we normally calculate:

$$\Delta E = E_{ab}^{AB} - \left(E_a^A + E_b^B\right)$$

- Then we can determine the stabilisation energy when the extra basis sets are present by computing a in the geometry of ab using the AB basis, this is achieved by removing the "nuclei and electrons" from monomer b but leaving all the basis functions behind. E_a^{AB} is always more negative than E_a^A. These atom-less basis functions are refered to as "*ghost functions*". The same process can be followed for b to obtain:

$$E_{BSSE(a)} = E_a^{AB} - E_a^A$$
$$E_{BSSE(b)} = E_b^{AB} - E_b^B$$

- The BSSE then becomes

$$\begin{aligned}\Delta E^{CP} &= E_{ab}^{AB} - \left(E_a^A + E_{BSSE(a)} + E_b^B + E_{BSSE(b)}\right)\\ &= E_{ab}^{AB} - \left(E_a^A + (E_a^{AB} - E_a^A) + E_b^B + (E_b^{AB} - E_b^B)\right)\\ &= E_{ab}^{AB} - (E_a^{AB} + E_b^{AB})\end{aligned}$$

- The Counterpoise correction is not perfect. The CP can overcorrect, because when a is being computed with the basis set AB all the B functions are available, but in ab all the occupied orbitals are not available. This can be a particular problem for H-bonded complexes studied with small basis sets.
- In the above derivation we made an implicit assumption that there was not a large contribution due to the changing conformation of monomer a or b from the isolated system to the interacting system, this adds a further level of complexity.
- The more "monomers" you have the larger the BSSE, so how you split your system up can impact on the result. You can now have two body and three body interactions, then how do we sensibly account for these?
- This becomes a particular issue if you want to compute an intra-molecular BSSE, how do you divide the molecule up? You will also run into issues of charge and spin-state of the fragments.
- There are a number of further methods which attempt to evaluate BSSE for these more complex cases but these are beyond the scope of this course.
- The BSSE is zero at the limit of a complete basis. However we seldom have the resources to go to this level. For example, for the water dimer we should need a cc-pV5Z basis set (574 basis functions) at the MP2 level. However it known that for basis sets of triple-ζ quality BSSE is reduced to about 10%. Nevertheless the problem still arrises if we want to calculate structures with more atoms, we must use lower level basis sets and then the BSSE is an issue.
- Another problem arrises with respect to geometry optimisation. Almost exclusively the CP correction is applied to a non-CP corrected optimised geometry. However for a weakly bound system this may induce significant changes in intermolecular distances.

- Basis sets need to be *balanced*, that is each electron or orbital needs to be described equally well. This doesn't mean that each atom has exactly the same basis set. For example, using the same basis for Li and F in LiF, which is really Li^+ & F^-, means the basis set for Li^+ has more functions per electron than F^-, and thus the electrons of Li^+ are better described. To balance the basis set you should add a set of diffuse functions to the F atom.
- Many computational packages will actually allow you to use poor basis sets, and to produce an unbalanced basis. This is were untrained users have problems, as the package will still produce and answer, but it is a case of "garbage in, garbage out"!
- One way of reducing the cost of a calculation is to use better basis sets on the chemically active part of a system and then using poorer basis sets on the surroundings. Given the arguments above, it is clear, that you must be VERY careful when doing this as it is easy to create artefacts and incorrect results.

Basis Set Hierarchy

- OK, you say, why don't we max out the number of basis functions, have a t-aug-cc-QZ3P basis set? The simple answer is cost, most packages can handle more than 10000 primitive Gaussians, but the time taken to do a single cycle, and the cost in memory and disk to store the integral information can be extreme. A rough rule of thumb is that the computational effort grows as N^4 (up to N^7 for high level methods) where N is the number of basis functions. Thus if one cycle of your molecule using 100 primitive Gaussians takes 1second, then improving the basis set to use 10000 primitives would take ≈3 years per cycle. Memory is also required, an order of magnitude calculation has a 10000 basis job requiring ≈34GB, and higher level methods require more memory.
- In general the smaller the basis the poorer the description, and the larger the basis the better the description of a molecule. We measure how good a basis set is by how low we can get the energy. However, as a basis set improves the energy lowers by smaller and smaller amounts and gradually we move toward a limit where increasing the basis set makes a negligible decrease in the energy. We call this the "*basis set limit*", these basis sets are extremely large.
- Each computational method (eg HF, MP2, CCSD(T)) has its own basis set limit, and the better the method the more basis functions are required to reach the basis set limit. This convergence behaviour has been well studied and means that each method has a well known systematic basis set error. The Huzinaga & Dunning basis sets converge systematically to the basis set limit, the Pople basis sets do not.
- There is always an error due to the fact that a basis set cannot completely describe the relevant system (this would require infinite functions, and even then you would run into linear dependency problems) This error is called the "*basis set incompletemss error*" or BSIE.
- While the energy may converge with increasing basis set descriptions, properties do not follow this convergence behaviour. This means that it is very difficult to determine the error due to the basis set in a given

property. Basis sets, in this case, need to be added in a well informed and sensible way.

The Pople basis set range	**Huzinaga-Dunning basis set range**
STO-3G	VDZ
3-21G	VTZ
4-31G	VQZ
6-31G(d)	cc-pVDZ
6-31G(d,p)	aug-cc-pVDZ
6-311G(2df,2pd)	aug-cc-pcVDZ
	cc-pVTZ
	aug-cc-pVTZ
	aug-cc-pcVDZ
	cc-pVQZ
	aug-cc-pVQZ
	aug-cc-pcVQZ

- In the table above I have listed a hierarchy of common basis sets, note that the Pople basis sets are generally of a lower quality than the Huzinaga & Dunning, so that the 6-31G ≈ VDZ while the 6-311G ≈ VTZ etc.
- Properties that depend on the electric field, or distortion of the electron-density require a good description of the tail of the orbitals and thus need diffuse and polarization functions. Properties that depend on the magnetic field, nuclear spin, and core electron density need tight functions and orbitals with a well defined core region.
- We have to compromise within the limits of our computational resources. In reality most calculations of larger inorganic systems are carried out at the HF, DFT, MP2 level with a medium level basis set 6-311+G(d,p) in terms of the Pople type basis and cc-pVDZ or cc-pVTZ in terms of the Huzinaga & Dunning type basis.

Basis	r(OH)	α(HOH)
cc-pVDZ	0.9463	104.61
cc-pVTZ	0.9406	106.00
cc-pVQZ	0.9396	106.22
cc-pV5Z	0.9396	106.33
cc-pV6Z	0.9396	106.33

Table 1 H_2O geometry as a function of basis set at the HF level

Basis	r(OH)	α(HOH)
cc-pVDZ	0.9649	101.90
cc-pVTZ	0.9591	103.59
cc-pVQZ	0.9577	104.02
cc-pV5Z	0.9579	104.29
cc-pV6Z	0.9581	104.36

Table 2 H_2O geometry as a function of basis set at the MP2 level

Pseudo-Potentials

- Pseudo-potentials (PP), otherwise known as Effective Core Potentials (ECP) are essential to describing atoms with a large number of electrons at a reasonable cost.
- As atoms get larger the core electrons get further away from the active valence electrons, and their participation in bonding can become minimal. However we still require a large number of Gaussian functions to describe the core electrons. In addition for elements below the 3rd row, the inner electrons experience a large core charge and are accelerated to near the speed of light and a relativistic correction is

required. To include the relativistic terms in the Hamiltonian would be very expensive.

- Previously we discussed replacing the core electrons by a set of contracted Gaussians, where only one variable parameter is left. Now we are replacing the core electrons by a set of frozen functions. Typically a set of Gaussians is given for each angular momentum component.
- As with the development of basis sets creating PP is a complex, exacting and delicate task. For a group of chemists/physicists it is the primary component of their research career. One key point is that you *cannot use any basis set with a PP*, you must use the basis set constructed for use with that particular PP.
- Many PP and their accompanying basis sets are often already contained within libraries attached to your favourite computational code. In fact, it is better to use these libraries as you are likely to make an error when entering the details by hand. Common pseudo-potentials include:

Los Alamos ECPs of Hay and Wadt
CEP ECPs of Stevens/Basch/Krauss
Stuttgart/Dresden ECPs
Goddard/Smedley ECP