The Wave equation

- The theoretical foundation for quantum chemistry is the time-independent Schrödinger wave equation:

$$\hat{H}\Psi = E\Psi$$

- Ψ is the Wavefunction. It is a function of the positions of all the fundamental particles (electrons and nuclei) in the system.
- $\hat{H}$ is the Hamiltonian operator. It is the operator associated with the observable energy.
- E is the Total Energy of the system. It is a scalar (number).
- Relativistic effects are usually small and will be ignored.

- The Hamiltonian, $\hat{H}$, is an operator. It contains all the terms that contribute to the energy of a system:

$$\hat{H} = \hat{T} + \hat{V}$$

- $\hat{T}$ is the kinetic energy operator:

$$\hat{T} = \hat{T}_e + \hat{T}_n$$

$$\hat{T}_e = -\frac{1}{2}\sum_i \nabla_i^2 \qquad \hat{T}_n = -\frac{1}{2M_A}\sum_A \nabla_A^2$$

- ∇^2 is the Laplacian given by: $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

The Hamiltonian

- $\hat{V}$ is the potential energy operator:

$$\hat{V} = \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee}$$

- $\hat{V}_{nn}$ is the nuclear-nuclear repulsion term:

$$\hat{V}_{nn} = \sum_{A<B} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}$$

- $\hat{V}_{ne}$ is the nuclear-electron attraction term:

$$\hat{V}_{ne} = -\sum_{iA} \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|}$$

- $\hat{V}_{ee}$ is the electron-electron repulsion term:

$$\hat{V}_{ee} = \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Atomic units

All quantum chemical calculations use a special system of units which, while not part of the SI, are very natural and greatly simplify expressions for various quantities.

- The length unit is the bohr ($a_0 = 5.29 \times 10^{-11}$m)
- The mass unit is the electron mass ($m_{\mathrm{e}} = 9.11 \times 10^{-31}$kg)
- The charge unit is the electron charge ($e = 1.60 \times 10^{-19}$C)
- The energy unit is the hartree ($E_{\mathrm{h}} = 4.36 \times 10^{-18}$J)

For example, the energy of the H atom is $\frac{-1}{2}$ hartree (exactly). In more familiar units this is $-1,313$ kJ/mol.

The hydrogen atom
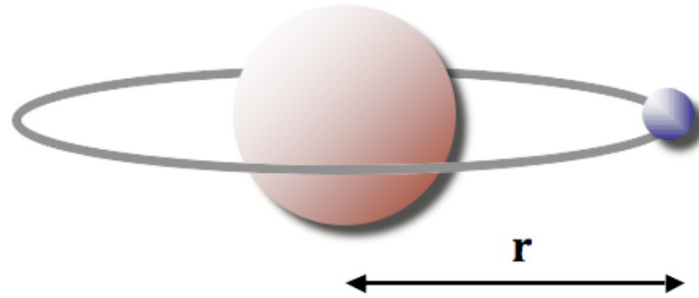
- We will use the nucleus as the centre of our coordinates.
- The Hamiltonian is then given by:

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee}$$
$$= -\frac{1}{2}\nabla_r^2 - \frac{1}{r}$$

- The ground-state wavefunction is simply a function of r.

The chemical connection

- So far we have focused mainly on obtaining the total energy of our system.

- Many chemical properties can be obtained from derivatives of the energy with respect to some external parameter.

- Examples of external parameters include:
  - Geometric parameters (bond lengths, angles *etc.*).
  - Applied electric fields (*e.g.* from a solvent)
  - Magnetic field (in NMR experiments).

- 1st and 2nd derivatives are commonly available and used.

- Higher derivatives are required for some properties, but are expensive (and difficult!) to compute.

Hartree-Fock theory

- HF theory is the simplest wavefunction-based method.
- It relies on the following approximations:
  - The Born-Oppenheimer approximation
  - The independent electron approximation
  - The linear combination of atomic orbitals approximation
- The Hartree-Fock model introduces an intrinsic error called the correlation energy.
- It forms the foundation for more elaborate electronic structure methods.

The Born-Oppenheimer approximation

- Nuclei are much heavier than electrons (the mass of a proton $\approx$ 2000 times that of an electron) and therefore travel much more slowly.
- We assume the electrons can react instantaneously to any motion of the nuclei (think of a fly around a rhinoceros).
- This means the nuclei are stationary w.r.t. the electrons.
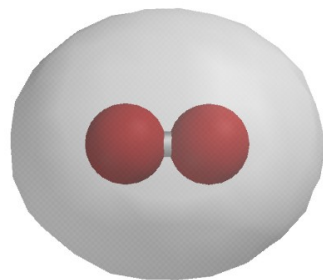- This assumption allows us to factorise the wave equation:

$$\Psi(\mathbf{R}, \mathbf{r}) = \Psi_n(\mathbf{R})\Psi_e(\mathbf{r}; \mathbf{R})$$

  where the ';' notation indicates a parametric dependence.
- The potential energy surface is a direct consequence of the BO approximation.

Consider the H_2 molecule:

- The total wavefunction involves 4x3 spatial coordinates:

$$\Psi = \Psi(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}_1, \mathbf{r}_2)$$

- We invoke the Born-Oppenheimer approximation:

$$\Psi = \Psi_n(\mathbf{R}_1, \mathbf{R}_2)\Psi_e(\mathbf{r}_1, \mathbf{r}_2)$$

- How do we model $\Psi_e(\mathbf{r}_1, \mathbf{r}_2)$?

The Hartree wavefunction

- We assume the wavefunction can be written as a Hartree product: $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$

- The individual one-electron wavefunctions, ψ_i are called molecular orbitals.

- This form of the wavefunction does not allow for instantaneous interactions of the electrons.

- Instead, the electrons feel the average field of all the other electrons in the system.

- The Hartree form of the wavefunction is is sometimes called the independent electron approximation.

The Pauli principle

- One of the postulates of quantum mechanics is that the total wavefunction must be antisymmetric with respect to the interchange of electron coordinates.

- Antisymmetry is a consequence of the Pauli Principle.

- The Hartree wavefunction is not antisymmetric:

$$\Psi(\mathbf{r}_2, \mathbf{r}_1) = \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1) \neq -\Psi(\mathbf{r}_1, \mathbf{r}_2)$$

- We can make the wavefunction antisymmetric by adding all signed permutations:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)\right]$$

The Hartree-Fock wavefunction

- The antisymmetrised Hartree wavefunction is called the Hartree-Fock wavefunction.

- It can be written as a Slater determinant:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \cdots & \psi_N(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \cdots & \psi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{r}_N) & \psi_2(\mathbf{r}_N) & \cdots & \psi_N(\mathbf{r}_N) \end{vmatrix}$$

- This ensures the electrons are indistinguishable and are therefore associated with every orbital!

- A Slater determinant is often written as $|\psi_1, \psi_2, \ldots \psi_N\rangle$
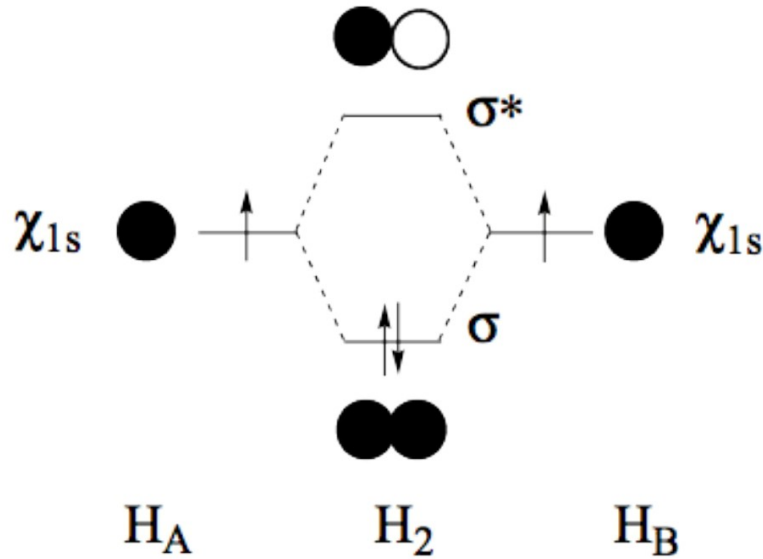
The LCAO approximation

- The HF wavefunction is antisymmetric and written in terms of the one-electron molecular orbitals (MOs).

- What do the MOs look like?

- We write them as a linear combination of atomic orbitals:

$$\psi_i(\mathbf{r}_i) = \sum_\mu C_{\mu i} \chi_\mu(\mathbf{r}_i)$$

- The χ_μ are atomic orbitals or basis functions.
- The $C_{\mu i}$ are MO coefficients.

The H_2 molecule:

$$\psi_1 = \sigma = \frac{1}{\sqrt{2}}\left(\chi_{1s}^A + \chi_{1s}^B\right)$$

$$\psi_2 = \sigma^* = \frac{1}{\sqrt{2}}\left(\chi_{1s}^A - \chi_{1s}^B\right)$$

- For H_2 the MO coefficients, $C_{\mu i}$, are $\pm\frac{1}{\sqrt{2}}$

The HF theory

- If Ψ is normalised, the expectation value of the energy is given by: $E = \langle \Psi | \hat{H} | \Psi \rangle$
- For the HF wavefunction, this can be written:

$$E_{\mathrm{HF}} = \sum_i H_i + \frac{1}{2} \sum_{ij} (J_{ij} - K_{ij})$$

- H_i involves one-electron terms arising from the kinetic energy of the electrons and the nuclear attraction energy.
- J_{ij} involves two-electron terms associated with the coulomb repulsion between the electrons.
- K_{ij} involves two-electron terms associated with the exchange of electronic coordinates.

The HF energy

- Remember that our wavefunction is given in terms of a determinant: $|\psi_1, \psi_2, \ldots \psi_N\rangle$
- And our MOs are written as a LCAO:

$$\psi_i(\mathbf{r}_i) = \sum_\mu C_{\mu i} \chi_\mu(\mathbf{r}_i)$$

- We can write the one-electron parts of the energy as:

$$\begin{aligned} H_i &= \langle \psi_i | \hat{\mathbf{h}} | \psi_i \rangle \\ &= \sum_{\mu\nu} C_{\mu i} C_{\nu i} \langle \chi_\mu | \hat{\mathbf{h}} | \chi_\nu \rangle \end{aligned}$$

- The J_{ij} and K_{ij} matrices can also be written in terms of the MO coefficients, $C_{\mu i}$.

The variational principle

- The MO coefficients, $C_{\mu i}$, can be determined using the variational theorem:

Variational Theorem

The energy determined from any approximate wavefunction will always be greater than the energy for the exact wavefunction.

- The energy of the exact wavefunction serves as a lower bound on the calculated energy and therefore the $C_{\mu i}$ can be simply adjusted until the total energy of the system is minimised. This is the variational method.

The self-consistent field method

- Consider a 2-electron system with MOs $\psi_1(\mathbf{r}_1)$ and $\psi_2(\mathbf{r}_2)$.
- Electron 1 feels the nuclei and the field of $\psi_2(\mathbf{r}_2)$.
- Electron 2 feels the nuclei and the field of $\psi_1(\mathbf{r}_1)$.
- This creates a chicken and egg situation: we need ψ_2 to solve for ψ_1, but we need ψ_1 to solve for ψ_2.

The SCF Process

1. Guess a set of MOs, $C_{\mu i}$
2. Use MOs to compute H_i, J_{ij} and K_{ij}
3. Solve the HF equations to obtain a new set of MOs
4. Are the new MOs different? Yes $\rightarrow$ (2) : No $\rightarrow$ (5)
5. Self-consistent field converged

Electron spin

- So far for simplicity we have ignored the spin variable, ω.
- Each MO actually contains a spatial part and a spin part.
- For each spatial orbital, there are two spin orbitals:
  $\chi_i^\alpha(\mathbf{r}, \omega) = \psi_i(\mathbf{r})\alpha(\omega)$ and $\chi_i^\beta(\mathbf{r}, \omega) = \psi_i(\mathbf{r})\beta(\omega)$.
- This is reasonable for closed-shell systems, but not for open-shell systems.

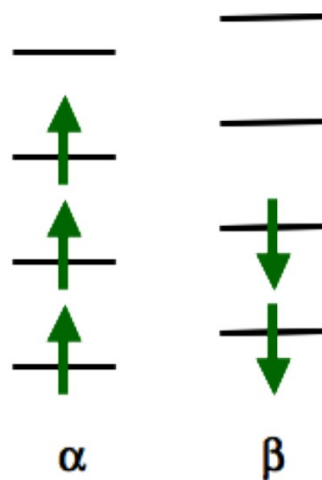H_2 H_2^-
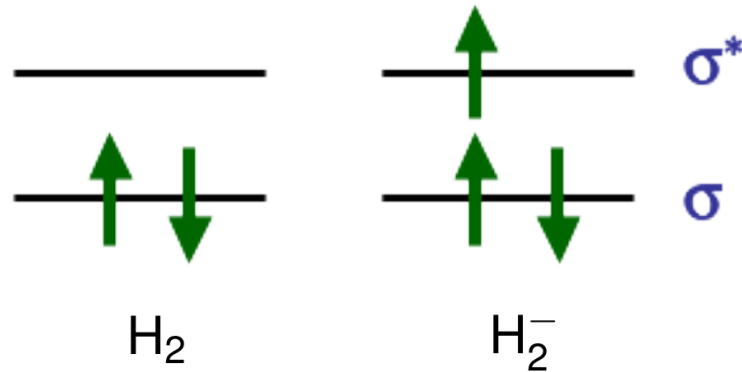
Restricted and unrestricted HF theory

RHF
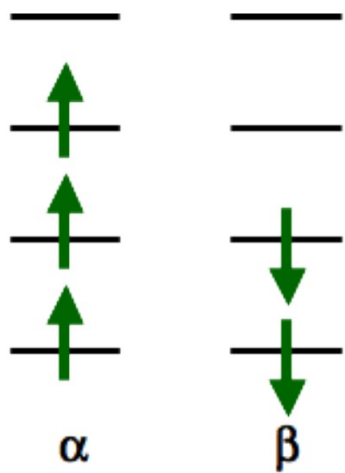
UHF

The spatial part of the spin orbitals are the same:

$$\phi_i^\alpha = \phi_i^\beta$$

The spatial part of the spin orbitals are different:
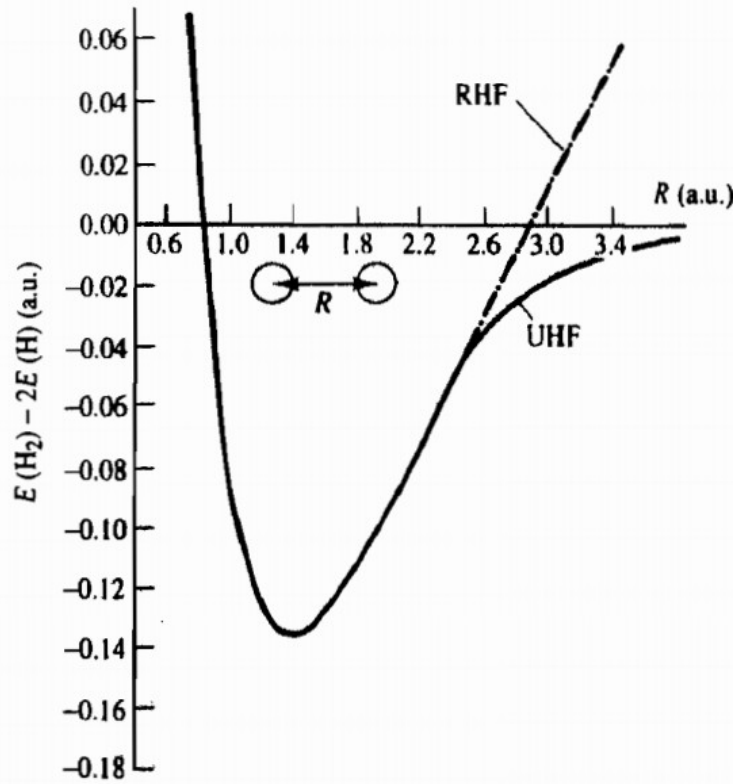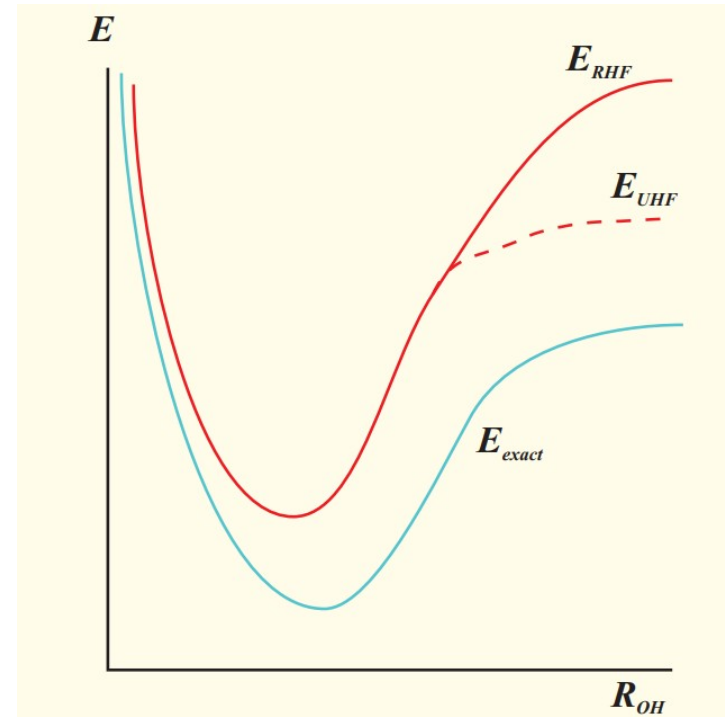
$$\phi_i^\alpha \neq \phi_i^\beta$$

RHF versus UHF

Fig. 2.9 UHF and RHF dissociation curves for H_2.

The dissociation curves of water molecule

Pros and cons

Advantages of the UHF method:

- The UHF wavefunction has more flexiblity and can give a lower energy (variationally better).
- Provides a qualitatively correct description of bond-breaking.
- Provides a better model for systems with unpaired electrons.

Disadvantages of the UHF method:

- Calculations take slightly longer to perform than for RHF.
- Can lead to spin-contamination which means the wavefunction is no longer a spin-eigenfunction (as it should be).

Performance: HF equilibrium bond lengths

Table 1: Hartree-Fock and experimental equilibrium bond lengths R_e (in pm)

Molecule	Bond	HF	Experiment
H_2	R_{HH}	73.4	74.1
HF	R_{FH}	89.7	91.7
H_2O	R_{OH}	94.0	95.7
O_3	R_{OO}	119.2	127.2
CO_2	R_{CO}	113.4	116
C_2H_4	R_{CC}	131.3	133.4
CH_4	R_{CH}	108.2	108.6

Hartree-Fock calculations systematically underestimate equilibrium bond lengths

Performance: HF atomization energy

Table 2: Hartree-Fock and experimental electronic atomization energies (kJ/mol)

Molecule	HF	Experiment
F_2	-155.3	163.4
H_2	350.8	458.0
HF	405.7	593.2
H_2O	652.3	975.3
O_3	-238.2	616.2
CO_2	1033.4	1632.5
C_2H_4	1793.9	2359.8
CH_4	1374.1	1759.3

Hartree-Fock calculations systematically underestimate atomization energies.

Performance: HF reaction enthalpies

Table 3: Hartree-Fock and experimental electronic reaction enthalpies (kJ/mol)

Reaction	HF	Experiment
$CO + H_2 \rightarrow CH_2O$	2.7	-21.8
$H_2O + F_2 \rightarrow HOF + HF$	-139.1	-129.4
$N_2 + 3H_2 \rightarrow 2NH_3$	-147.1	-165.4
$C_2H_2 + H_2 \rightarrow C_2H_4$	-214.1	-203.9
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	-242.0	-245.3
$2CH_2 \rightarrow C_2H_4$	-731.8	-845.7
$O_3 + 3H_2 \rightarrow 3H_2O$	-1142.7	-935.5

Hartree-Fock method fails when reaction is far from isodesmic.

Lack of electron correlations!!

Electron correlation

Angular part of He ground state wavefunction
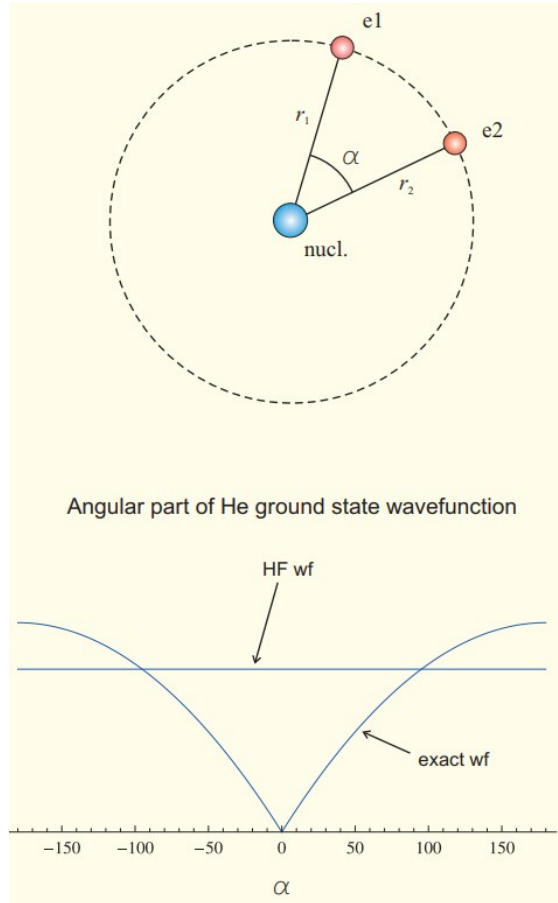
- In the Hartree-Fock model, the repulsion energy between two electrons is calculated between an electron and the average electron density for the other electron. What is unphysical about this is that it doesn't take into account the fact that the electron will push away the other electrons as it moves around. This tendency for the electrons to stay apart diminishes the repulsion energy.
- If one is on one side of the molecule, the other electron is likely to be on the other side.
- Their positions are correlated, an effect not included in a Hartree-Fock calculation.
- While the absolute energies calculated by the Hartree-Fock method are too high, relative energies may still be useful.

Basis sets

- The atom-centred functions used to describe the atomic orbitals are known as basis functions and collectively form a basis set.

- Larger basis sets give a better approximation to the atomic orbitals as they place fewer restrictions on the wavefunction.

- Larger basis sets attract a higher computational cost.

- Standard basis sets are carefully designed to give the best description for the lowest cost.

Minimal basis sets

- The simplest possible atomic orbital representation is called a minimal basis set.

- Minimal basis sets contain one basis functions for each occupied atomic orbital.

- For example:
  - H & He   1 function ($1s$)
  - 1st row   5 functions, ($1s, 2s, 2p_x, 2p_y, 2p_z$)
  - 2nd row   9 functions, ($1s, 2s, 2p_x, 2p_y, 2p_z, 3s, 3p_x, 3p_y, 3p_z$)

- Functions are always added in shells., *e.g.* a p shell consists of three functions.

Minimal basis sets

- The STO-3G basis set is a minimal basis set where each atomic orbital is made up of 3 Gaussians.

- The STO-6G basis set is a minimal basis set where each atomic orbital is made up of 6 Gaussians.

- Minimal basis sets are not well suited to model the anisotropic effects of bonding.

- Basis function exponents do not vary and therefore the orbitals have a fixed size and cannot expand or contract.

Split valence basis sets

- Split-valence basis sets model each valence orbital by two or more basis functions that have different exponents.
- They allow for size variations that occur in bonding:
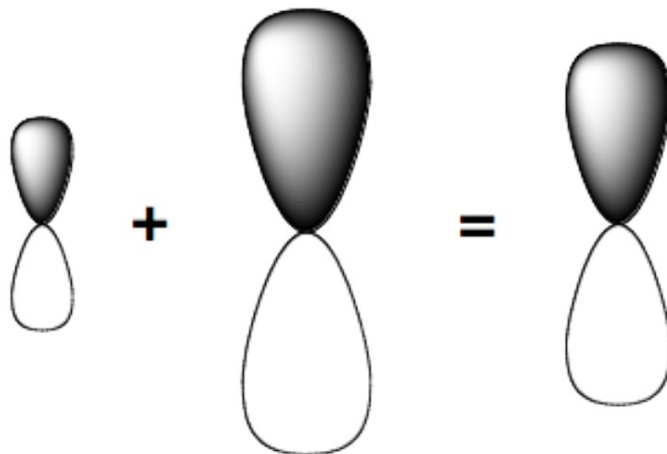
- Double split valence basis sets: 3-21G, 6-31G and VDZ
- Triple split valence basis sets: 6-311G and VTZ

Example: Carbon 6-31G basis set

```
C    0
S    6   1.00
        3047.52490              0.183470000E-02
        457.369510              0.140373000E-01
        103.948690              0.688426000E-01
        29.2101550              0.232184400
        9.28666300              0.467941300
        3.16392700              0.362312000
SP   3   1.00
        7.86827240             -0.119332400         0.689991000E-01
        1.88128850             -0.160854200         0.316424000
        0.544249300             1.14345640          0.744308300
SP   1   1.00
        0.168714400             1.00000000          1.00000000
```

Polarized basis sets

- Polarisation functions have higher angular momentum than the occupied AOs.
- They allow for anisotropic variations that occur in bonding
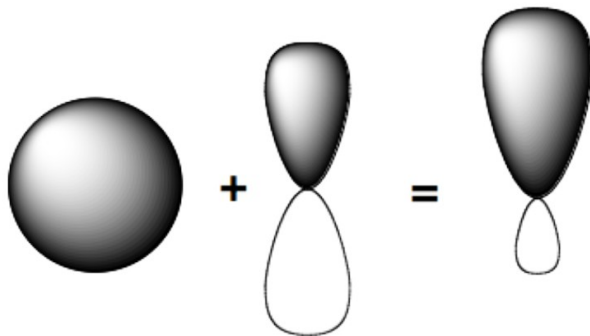
- 6-31G(d) or 6-31G* include d functions on the heavy atoms (non-hydrogen).
- 6-31G(d, p) or 6-31G** include d functions on heavy atoms and p functions on hydrogen atoms.

Diffuse functions

- Diffuse basis functions are additional functions with small exponents, and are therefore have large spatial extent.
- They allow for accurate modelling of systems with weakly bound electrons, such as:
  - Anions
  - Excited states
- A set of diffuse functions usually includes a diffuse s orbital and a set of diffuse p orbitals with the same exponent.
- Examples include 6-31+G which has diffuse functions on the heavy atoms and 6-31++G which has diffuse functions on hydrogen atoms as well.

Mix and match

- Larger basis sets can be built up from these components, for example 6-311++G(2df,2pd).

- Dunning basis sets also exist, for example pVDZ and pVTZ (polarised double split valence and triple split valence, respectively).

- Some basis sets work better for HF and DFT calculations (*e.g.* Pople basis sets and Jensen's pc-n bases)

- Others are best for correlated calculations (*e.g.* cc-pV*Z).

- Carefully designed sequences of basis sets can be used to extrapolate to the basis set limit. For example cc-pVDZ, cc-pVTZ, cc-pVQZ...

Effective core potentials

- Effective Core Potentials replace core electrons with an effective potential which is added to the Hamiltonian.
- ECPs have two main advantages:
  - They reduce the number of electrons (cheaper).
  - They can be parameterised to take account of relativity.
- Non-relativistic ECPs include HWMB (STO-3G) and LANL2DZ (6-31G).
- Relativistic ECPs include SRSC (6-311G*) and SRLC (6-31G).
- The size of the core can vary, for example:
  SRLC (large core): K = [Ar] + $3s$, $2p$
  SRSC (small core): K = [Ne] + $5s$, $4p$
- ECPs are particularly useful for transition metals.

Counting basis functions

It is important to have an idea of how many basis functions are in your molecule as this will determine the cost of the calculation.

Basis set	Description	H	C,O	H_2O	C_6H_6
STO-3G	Minimal	1	5	7	36
3-21G	Double split-valence	2	9	13	66
6-31G(d)	Double split-valence with polarisation	2	15	19	102
6-31G(d, p)	Ditto, with p functions on H	5	15	25	120
6-311+G(d, p)	Triple split-valence with polarisation, p functions on H and diffuse functions on heavy atoms	6	22	34	168

Accuracy

The accuracy of the computed properties is sensitive to the quality of the basis set. Consider the bond length and dissociation energy of the hydrogen fluoride molecule:

Basis set	Bond Length (Å)	D_0 (kJ/mol)
6-31G(d)	0.9337	491
6-31G(d,p)	0.9213	523
6-31+G(d)	0.9408	515
6-311G(d)	0.9175	484
6-311+G(d,p)	0.9166	551
Expt.	0.917	566

ZPVE = 25 kJ/mol MP2/6-311+G(d,p)

Basis set superposition error

Calculations of interaction energies are susceptible to basis set superposition error (BSSE) if they use finite basis sets.

- As the atoms of interacting molecules or two molecules approach one another, their basis functions overlap. Each monomer "borrows" functions from other nearby components, effectively increasing its basis set and improving the calculation.
- The counterpoise approach (CP) calculates the BSSE employing "ghost orbitals". In the uncorrected calculation of a dimer AB, the dimer basis set is the union of the two monomer basis sets. The uncorrected interaction energy is

$$V_{AB}(G) = E_{AB}(G, AB) - E_A(A) - E_B(B)$$

where G denotes the coordinates that specify the geometry of the dimer and $E_{AB}(G, AB)$ the total energy of the dimer AB calculated with the full basis set AB of the dimer at that geometry. Similarly, $E_A(A)$ and $E_B(B)$ denote the total energies of the monomers A and B, each calculated with the appropriate monomer basis sets A and B, respectively.

Basis set superposition error

The counterpoise corrected interaction energy is

$$V_{AB}^{cc}(G) = E_{AB}(G, AB) - E_A(G, AB) - E_B(G, AB)$$

where $E_A(G, AB)$ and $E_B(G, AB)$ denote the total energies of monomers A and B, respectively, computed with the dimer basis set at geometry G, i.e. in the calculation of monomer A the basis set of the "other" monomer B is present at the same location as in dimer A, but the nuclei of B are not. In this way, the basis set for each monomer is extended by the functions of the other monomer. The counterpoise corrected energy is thus

$$E_{AB}^{cc} = E_{AB}(G, AB) + V_{AB}^{cc}(G) - V_{AB}(G)$$

BSSE is present in all molecular calculations involving finite basis sets but in practice its effect is important in calculations involving weakly bound complexes. Usually its magnitude is few kJ/mol to binding energies which is often very significant.