

## Ab Initio Calculations

*Ab initio* means 'from the beginning' and these calculations compute chemical structures, properties and reactivities from a purely theoretical first principles approach. The only inputs required for the calculation are the speed of light ( $c$ ), Planck's constant ( $h$ ), the electronic mass ( $m_e$ ), the electronic charge ( $q_e$ ) and a chemical structure.

The underlying mathematics of *ab initio* methods are complex but a detailed knowledge is not needed to be able to understand and use the methods effectively.

### Hartree-Fock Theory

In the Hartree-Fock (HF) method, the  $n$ -electron Schrödinger equation is effectively replaced by  $n$  1-electron Schrödinger equations (the HF equations).

$$F_i \phi_i = \varepsilon_i \phi_i$$

Where  $\phi_i$  are the HF molecular orbitals,  $\varepsilon_i$  the energy of orbital  $i$  and  $F_i$  is the Fock operator

$$F_i = -\frac{1}{2} \nabla_i^2 - \sum_{\alpha=1}^N \frac{Z_{i\alpha}}{r_{i\alpha}} + \sum_{j \neq i} [2J_{ij} - K_{ij}]$$

$$J_{ij} = \int \phi_i(1) \phi_j(2) \frac{1}{r_{12}} \phi_i(1) \phi_j(2) d\tau_{12}$$

$$K_{ij} = \int \phi_i(1) \phi_j(2) \frac{1}{r_{12}} \phi_i(2) \phi_j(1) d\tau_{12}$$

The details of these equations are not really important. What is important is that we seem to require the orbitals (in  $J$  and  $K$ ) to solve the HF equations to yield the orbitals!?!?

This is where the self-consistent field (SCF) approach comes in:

1. Begin with a set of guess orbitals,  $\{\phi_i\}^{(0)}$ .
2. Calculate a new set of orbitals,  $\{\phi_i\}^{(1)}$ , using the HF equations. These should be an improvement on the starting set.
3. Use the new, improved orbitals  $\{\phi_i\}^{(1)}$ , in the HF equations to generate a third set,  $\{\phi_i\}^{(2)}$  (which will improve on the second set).
4. Repeat this process until a convergence criterion, based on the energies or orbitals, is met.

The  $[2J_{ij} - K_{ij}]$  term in the HF equations represents, for an electron in orbital  $\phi_i$ , the effective electrostatic field due to the electrons in all the other orbitals. The iterative process is thus continued until the effective field remains unchanged – hence the term SCF.

### Electron Correlation

The HF method does not take full account of the interelectronic repulsion term from the full electronic Schrödinger equation. The remaining part of this term is

known as *electron correlation* and we can define the correlation energy as the difference between the energy of the HF wavefunction and the true non-relativistic energy. To approach the 'true' electronic wavefunction (and hence a better solution to the Schrödinger equation) then electron correlation must be taken into account.

As mentioned above, some form of electron correlation is also needed to provide a realistic description of dissociation processes.

A description of the theory behind the methods used to include electron correlation is beyond the scope of this introduction and so we will limit ourselves to a description of the methods and their practical uses. If you want to find out more, refer to the web or the books listed in the references.

Density functional theory (DFT) also includes a degree of electron correlation.

All of these methods are also known as post-HF methods.

### **Moller-Plesset Perturbation Theory (MP2, MP3, MP4)**

The name comes from the basic principle of the method: in the system, electrons are "perturbated", or moved from a ground state to an excited state, and then allowed to fall back down to the ground state.

1. Calculate HF wavefunctions (electrons in ground state)
2. Move some electrons to excited state
3. Calculate wavefunctions of electrons in excited states
4. Mix ground and excited states together

There are several levels of the MP theory, indicated by the number following the abbreviation "MP", as in MP2, MP3, etc..

MP2 methods are routinely applied to single molecule calculations on molecules with less than 20 atoms and may be possible for larger systems. MP2 gives excellent results where the HF wavefunction is close to the full wavefunction (e.g. close to the equilibrium geometry) but can do less well for bond breaking processes.

### **Configuration Interaction (CI, CISD)**

If we could use a full CI treatment then we would have an exact solution to the electronic Schrödinger equation. Unfortunately, any sort of reasonable CI treatment is prohibitively computationally expensive for all but the smallest of molecular systems.

CI methods (such as CISD) have the advantage that they describe bond-breaking and bond-forming processes very well indeed, include a large degree of the missing electron correlation and are able to describe multiple electronic states simultaneously (giving access to information about electronic transitions.) Traditionally, they have been regarded as the 'gold-standard' of *ab initio* methods.

### **Multi-configuration SCF (MCSCF, CASSCF)**

This method is related to the CI treatment and is used for describing excited electronic states and high-accuracy studies of dissociative processes. As for CI, it is prohibitively expensive for everything but smaller molecular systems.

## Coupled Cluster Theory (CCSD, CCSD(T))

Coupled cluster calculations work in a similar way to both CI and MCSCF treatments but tend to recover more of the electron correlation than either of those methods for the same amount of computational effort. In recent years it has replaced CI as the 'gold-standard' of *ab initio* calculations.

As for CI and MCSCF, CC is only practical for small molecules.

### Some Practical Notes

A list of the various *ab initio* methods and practical notes about their use and applicability.

Method	System Size (atoms)	Good for...	Bad for...
HF	<100	+ Equilibrium geometries + Equilibrium frequencies + Relative energies of conformations	– Dissociative processes – Structures far from equilibrium
MP2	<50	+ Transition state calculations + Free radicals + Vibrational frequencies	– (Dissociative processes) – Structures with excited state character
CISD	<10	+ High accuracy + Electronic excitations	– Medium to large molecules
MCSCF	<20	+ Structures with excited state character + Dissociative processes	– Large molecules
CCSD(T)	<20	+ High accuracy + Dissociative processes	– Large molecules – Electronic excitations

Generally, for systems that are commonly encountered experimentally, the only methods that are practical are HF or MP2 (DFT as well, see separate section). The higher quality methods are generally too computationally expensive unless you have access to very large computational resources. Even then, you may struggle to find software that can implement these methods and take advantage of the hardware.

### Advantages

*Ab initio* calculations are the most reliable computational methods available and provide descriptions of the electronic structure that are purely based in quantum mechanics. They provide predictions for properties that are completely devoid of any empirical bias. In addition, the methods are systematically improvable (unlike DFT methods) and we can rationally explain any differences between theory and experiment.

		Electron Correlation (Post-HF) →				Full CI	
		HF	MP2	MCSCF	CC/CI		
Basis Set	Minimal Multiple- $\zeta$ +Polarization +Diffuse					–	
	$\infty$						

### Disadvantages

The calculations can be intractable for larger systems, particularly when using post-HF methods.

There are difficulties using the more basic methods for studying chemical reactions.

### Applications

- Calculation and stability of structures: equilibrium, transition state and reaction intermediates.
- Characterization of the MOs – predictions of reactivity.
- Vibrational analysis – calculating IR and Raman spectra.
- Electronic transitions, CD response and characterization of excited states.
- Charge distribution and unpaired spin densities.

### Software Available on the EaStCHEM RCF

- **Gaussian 03** – All of the methods discussed above are available in the Gaussian suite of software. Gaussian is best suited to HF and MP2 calculations on molecules in the ground state.
- **MOLPRO** – As for Gaussian, all of the methods discussed above are available in the MOLPRO software package. MOLPRO is the software of choice for high level post-HF methods such as MCSCF, CC and CI.