Text book   Cramer: Essentials of Quantum Chemistry, Wiley (2 ed.)

## Chapter 3. Post Hartree-Fock methods (Cramer: chapter 7)

As discussed in the previous chapter. The aim is to develop **reliable** ab initio methods. The HF seldom is good enough and some computationally feasible improvements are needed.

There are many ways to improve the HF method. Most of them are very technical and in this course, the main ideas behind them are given. We can first "define" the correlation energy. The best (lowest) non-relativistic total energy within the Born-Oppenheimer approximation of the system is $E_{tot}$, the correlation energy is the difference

$$E_{corr} = E_{tot} - E_{HF} < 0$$

As such, this is not a very useful definition but if we have different well defined methods and basis sets to compute the correlation energy, the one which has the **lowest energy is the best**. The variational principle works also here.

The conceptually simplest post-HF method is the Configuration Interaction (CI) method. In this method the wave function is built from several determinants

$$\Psi(r_1,..r_N) = a_0\Psi^0 + \sum_{i,a} a_i^a\,\Psi_i^a + \sum_{ij,ab} a_{ij}^{ab}\,\Psi_{ij}^{ab} + ...$$

The new determinants are built form the HF orbitals but the electrons are also placed on exited states. The notation $\Psi_i^a$ means that one electron is excited from state i to state a, similarly $\Psi_{ij}^{ab}$ means that two electrons are excited from states i and j to states a and b. This wave function is denoted as CISD (CI with singlet and double excitations). The $\Psi^0$ is the Slater

determinant (or the HF wave functions). All the excited
determinants are **orthogonal** to the HF wf (and to each other).

Exercise: Show this.

In the CI calculations, the HF orbitals are kept constant and
the **a** coefficients are optimized. Again, the variational method
can be used

$$E_{CIS} = \min_a [\, a_0 \langle \Psi^0 | H | \Psi^0 \rangle + \sum_{i,a} a_i^a \langle \Psi^0 | H | \Psi_i^a \rangle ]$$

Or the matrix formalism can be used

$$H_{IJ} = \langle \Psi_i | H | \Psi_j \rangle$$

Where $\Psi_J$ mean any level of excited determinant. The matrix is
very big but mostly empty (sparse) and efficient handling of it
requires methods of sparse matrixes.

The CISD method is a reasonable solution for the correlation
energy for small molecules but for larger molecules, it become
rather inefficient. Also, for larger molecules CISD is not very
accurate and higher terms would be useful but methods like CISDT
become computationally very expensive. There will be a huge
amount of excitations to be computed. In general the pure CI
type methods become too expensive when the molecules size is
increasing. The best CI method is called Full CI or FCI. In
principle, it is an exact method but it is doable only for small
molecules.

For Full CI the number of determinant can be computed as

$$N_{det} = \binom{n}{k}^2$$

Where n is the number of orbital and k the number of electrons.
This grows very rapidly, when n=2k (and k is big)

$$N_{det} = \binom{2k}{k}^2 \approx \frac{16^k}{k\pi}$$

if k=10 $N_{det}$ = 3.4*10$^{10}$ !! This is very expensive to compute.

The formal computational scaling of different correlation methods. BUT with new codes like Orca (Turbomole, etc) this has changed a lot and both MP2 and CCSD(T) can be done with similar computational cost as HF. Note that there are small approximations in these faster methods.

| Scaling | Method | Real Scaling | note |
|---------|--------|-------------|------|
| $N^4$ | HF | $N^4$ | |
| $N^5$ | MP2 | $N^4$ (RI-MP2) | RI-MP2 is very reliable |
| $N^6$ | MP3, CISD, CCSD | $N^4$ for CCSD (DLPNO-CCSD) | method needs a lot of memory |
| $N^7$ | MP4, CCSD(T) | $N^4$ for CCSD(T) | method needs a lot of memory |
| $N^8$ | (MP5), CISDT, CCSDT | | |
| $N^{10}$ | (MP7), CISDTQ, CCSDTQ | | |

The CI has also a **size consistency problem**. This can be illustrated with an example of He dimer. The He atom have only two electrons and thus CISD is an exact method for it (CISD=FCI). When the $He_2$ is studied at CISD level the theory is not exact since the triple and quadrupole excitation are missing, (CISDTQ=FCI).
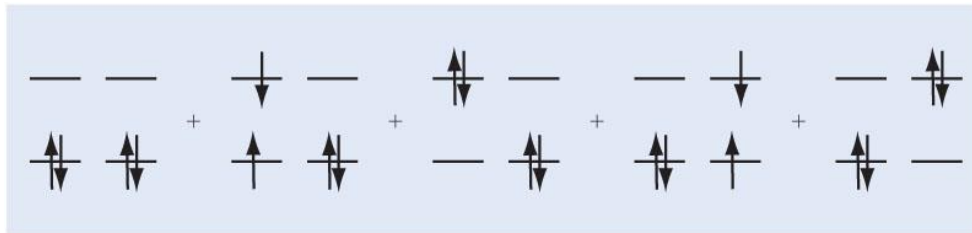
In general finite-CI accuracy reduce with the size of the molecule and any calculation which deals with molecules association is biased with the size consistency. This is a rather large problem for computational binding energies and an unfortunately feature for many Post-HF methods.

## Active Space SCF

Another approach to correlation is Active Space SCF. The first assumption is that not all possible excitations are needed. We can define limited amount of electrons and states in where all excitations are considered. This is called Complete Active Space (CAS). Then for larger amount of electrons and states only N excitations are allowed. This is Restricted Active Space (RAS).

Also the orbitals can be optimized for each excitation. This is called as Multi Reference method (MRSCF) (Note in CI the orbitals are not optimized). This causes more work but can significantly improve the total electronic energy.

In general, the CAS methods are quite easy to use. The good CAS depend strongly on the system. So testing is needed. There are also numerical problems related to the orbital optimizations. The CASSCF methods are not recommended for non-experts.

One can also combine the CI and the MR approach. The MRCI methods, like MRCISD, are not much used. They are expensive and probably difficult to use.
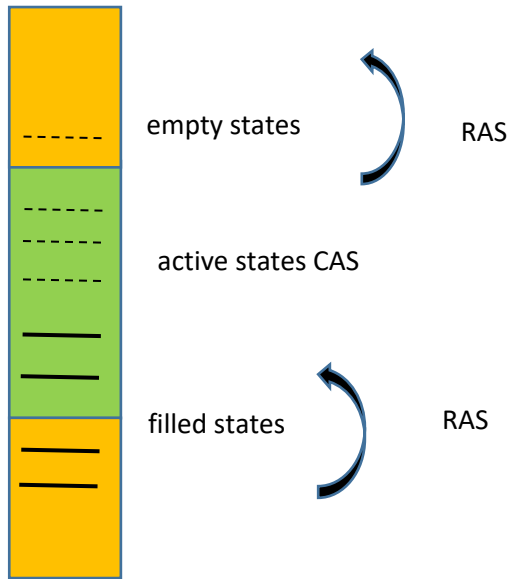
## Coupled Cluster method.

The Coupled Cluster Method is an advanced method to solve the CI
wave functions. The CC wave function is computed as

$$\Psi_{CC} = e^T \Psi_{HF}$$

where T=1+T$_1$+T$_2$+T$_3$+…, T$_n$ is an operator that makes n times excited
states. For example

$$T_2 = \sum_{ij,ab} t_{ij,ab}\, \tau_a^i \tau_b^j,$$

will make determinants that have two exited electrons. The
exponent of an operator is mathematically complex, but the main
point is that the CC wave functions are more complete than the
CI wf's. The CC wave functions have contributions like

$$\hat{C}\,\Psi_{HF} = e^T \Psi_{HF}$$

$$C_0 = 1, \qquad C_1 = T_1, \ \ C_2 = T_2 + \frac{1}{2}T_1^2, \ C_3 = T_3 + T_1 T_2 + \frac{1}{6}T_1^3$$

$$C_4 = T_4 + T_1 T_3 + \frac{1}{2}T_2^2 + \frac{1}{2}T_1^2 T_2 + \frac{1}{24}T_1^4$$

For example, at CCSD level we have only operators $T_1$ and $T_2$ we will have higher order terms in the $C_3$ and $C_4$ etc. level. The solution of the amplitudes is the trick. It can be done effectively. The CC is also size consistent which is a bonus compared to CI.

A good but far from easy presentation of CC can be found from *Helgaker, Jorgensen and Olsen: Molecular Electronic-Structure Theory* (Willey).

For practical point of view the CC is the best "black box" quantum chemistry methods there exists. CCSD is a good method and CCSDT and CCSDTQ are excellent methods but the later are expensive. Using perturbation method the triplet excitations can be treated more effectively and the CCSD(T) method is also a very reliable methods. In practice, it is often even better than CCSDT due to slight overestimation of the correlation. Today the CCSD(T) is considered the **"golden standard"** of quantum chemistry. This means that it is almost as accurate (for medium size molecules) as FCI or any other super accurate method but much cheaper. Compared to MRSCR methods the CC methods are easy to use and almost always reliable. Naturally the CCSD(T) is not cheap, but the new **DLPNO-CCSD(T)** is for larger systems are as fast as HF, so there is no reason not to do CCSD calculations!! (Providing you have enough memory for the calculations).

## Perturbation methods

Another approach to correlation it the perturbation methods. The idea is very general and it can be used to several other quantum chemical problems. We assume that we can solve Hamiltonian $H^{(0)}$ and the full Hamiltonian have a small perturbation V. The perturbation will be scale with parameter $\lambda$.

$$H = H^{(0)} + \lambda V$$

We can next write the energy and wave functions as a power series of $\lambda$.

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots \qquad \Psi_0 = \Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \cdots$$

Now we can write hierarchical equation for each power of $\lambda$

$$H^{(0)}\Psi_0^{(0)} = E^{(0)}\Psi_0^{(0)}$$

$$H^{(0)}\Psi_0^{(1)} + V\Psi_0^{(0)} = E^{(0)}\Psi_0^{(1)} + E^{(1)}\Psi_0^{(0)}$$

$$H^{(0)}\Psi_0^{(2)} + V\Psi_0^{(1)} = E^{(0)}\Psi_0^{(2)} + E^{(1)}\Psi_0^{(1)} + E^{(2)}\Psi_0^{(0)}$$

Note that notation $\Psi_0^{(n)}$ means the ground state wave function at perturbation level n. The different level wave functions are orthogonal $\left\langle \Psi_0^{(n)} \middle| \Psi_0^{(0)} \right\rangle = \delta_{n0}$.

So we can solve $E^{(1)}$, $\Psi^{(1)}$, $E^{(2)}$ etc.

$$E^{(1)} = \langle \Psi_0^{(0)} V \Psi_0^{(0)} \rangle \qquad E^{(2)} = \langle \Psi_0^{(0)} V \Psi_0^{(1)} \rangle \qquad \Psi_0^{(1)} = \sum_{n>0} \frac{\langle \Psi_n^{(0)} V \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \Psi_n^{(0)}$$

$$E^{(2)} = \sum_{n>0} \frac{\langle \Psi_n^{(0)} V \Psi_0^{(0)} \rangle^2}{E_0^{(0)} - E_n^{(0)}}$$

($\Psi_n^{(0)}$ means non-ground state wave function at iteration level 0).

The perturbation theory can be applied to correlation energy. This is called Moller-Plesset theory (MPn). Then the $H^{(0)}$ is the HF theory and the perturbation is

$$V = \sum_{i<j} \frac{1}{|r_i - r_j|} - \sum_{nm} (J_{nm} - \frac{1}{2} K_{nm})$$

This is clever since it corrects the HF error. The level (2) correction is

$$E^{(2)} = \sum_{i<j,a<b} \frac{[(ij|ab) - (ia|jb)]^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

The i,j denote occupied state and a,b unoccupied states. This the first real correction and it is called the MP2 theory. (The $E^{(0)} + E^{(1)}$ is in fact the HF energy). The perturbation theory can be computed to arbitrary level. The different levels are denotes as MPn. Of these, the most important is MP2. It is rather fast

and causes a significant correction to HF. The MP3 is a disappointment since it does not correct much the MP2. The MP4 is somewhat better but it is already very expensive. The higher terms are not used and in some model systems, it has been shown that the MPn series do not converge.

Below is convergence of the HF molecule with respect of the MPn series. The energies are related to the FCI energy. (Picture From Helgaker et al, Molecular Electronic-Structure Theory). The molecules eq distance is $R_e$ (so 2.5 $R_e$ is stretched molecule). As one can see the results are strange.
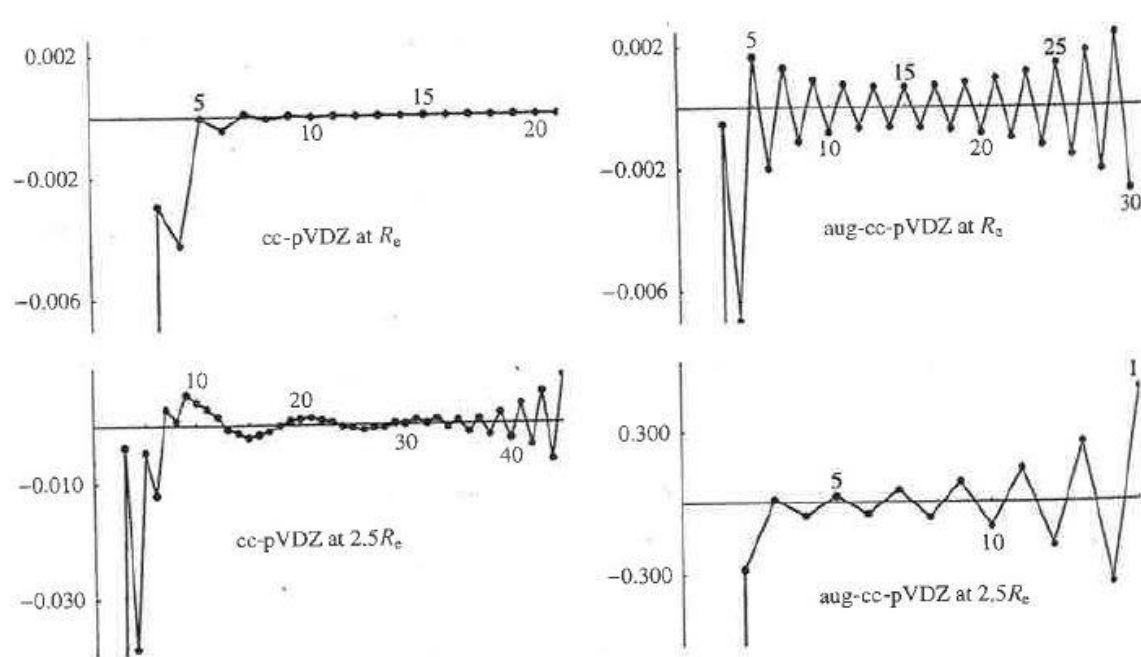


Fig. 14.6. Møller–Plesset expansions for the HF molecule. For each order in the perturbation series, we have plotted the difference between the Møller–Plesset energy and the corresponding FCI energy (in $E_h$).

Note the CC perturbation behaves better.


RI-approximation


Computationally the MP2 with small approximations can be implemented very effectively. The RI-MP2 method is much faster than and essentially as accurate as the true MP2. All practical

MP2 calculations for larger systems are done with RI-MP2 (or its variants). In big RI-MP2 calculations the most time consuming part is the HF.

The basic idea behind RI-MP2 is to fit the expensive double wave functions |ia) to **new (gaussian) basis functions |P)** (auxiliary basis). Now the expensive (ij|ab) term can be approximated

$(ij|ab) \approx \sum_{PQ}(ij|P)V_{PQ}(Q|ab)$  this is more complex but computationally faster. The (ij|ab) term scales as $N^4$ but (ij|P) as $N^3$ and $V_{QP}$ as $N^2$. The main point is that RI methods needs an additional basis which is not much larger than the original basis. Note that product of two gaussians (ij| is a Gaussian but the "size" of this basis is $N^2$ and nothing is gained. The (P| basis is almost as accurate as the product but much smaller.

The Orca input is simple  (version 4)

! RHF RI-MP2 TZVP AutoAux Opt

See also Orca Manual (3.0 page 41 to 42)

"You see that nothing is lost in the optimized geometry through the RI approximation thanks to the efficient and accurate RI-auxiliary basis sets of the Karlsruhe group (in general the deviations in the geometries between standard MP2 and RI-MP2 are very small). Thus, RI-MP2 really is a substantial improvement in efficiency over standard MP2."

The perturbation method is very general and it can used in several quantum chemical problems. One application is the CI and CC methods where the higher order excitations can be solved with perturbation theory. In the CCSD(T)WF's are solved in the CCSD level and the triplet corrections are done using the perturbation theory. The CCSD(T) method is the golden standard of quantum chemistry and it has the same scaling behavior as MP4.

Last, the basis set needed for well converged CI and MPn methods is larger than in the HF calculations. This is bad news since these post-HF methods have poorer scaling behavior than HF so the computations become quickly very time consuming.

Summary: **the MP2 method is a very important method for correlation.** It can be used for large molecules and it is a significant improvement to HF. The RI-method speedup the MP2

significantly. In Orca also the DLPNO-MP2 has been implemented. For medium size molecules it is roughly as fast as RI-MP2.

## DLPNO-CCSD(T) approximation

There is a lot of research focusing on development of the computational methods. In traditional quantum chemistry one area is on development fast computational algorithms for the known methods. The RI-type methods have improved the MP2 calculations a lot. The very new DLPNO-CCSD(T) development of Orca team is very interesting, it makes CCSD(T) level calculations possible for large molecules. (See more from Orca manual.) DLPNO means domain-based local pair natural orbital. In this method a pair natural orbitals are used and then localized, so that they can be classified into domains for proper sorting and selection of the most important excitations accounting for electronic correlation. This will reduce the computational cost a lot.

The latest implementation (2016, in Orca 4.0) has linear scaling !! For large systems (around 500 atoms) it is even faster than the HF. **So one can really use RI-MP2 (or DLPNO-MP2) or DLPNO-CCSD(T) for real problems**. But a small warning the **DLPNO-CCSD(T) method needs a lot of memory and the memory will come the bottleneck for large calculations.**
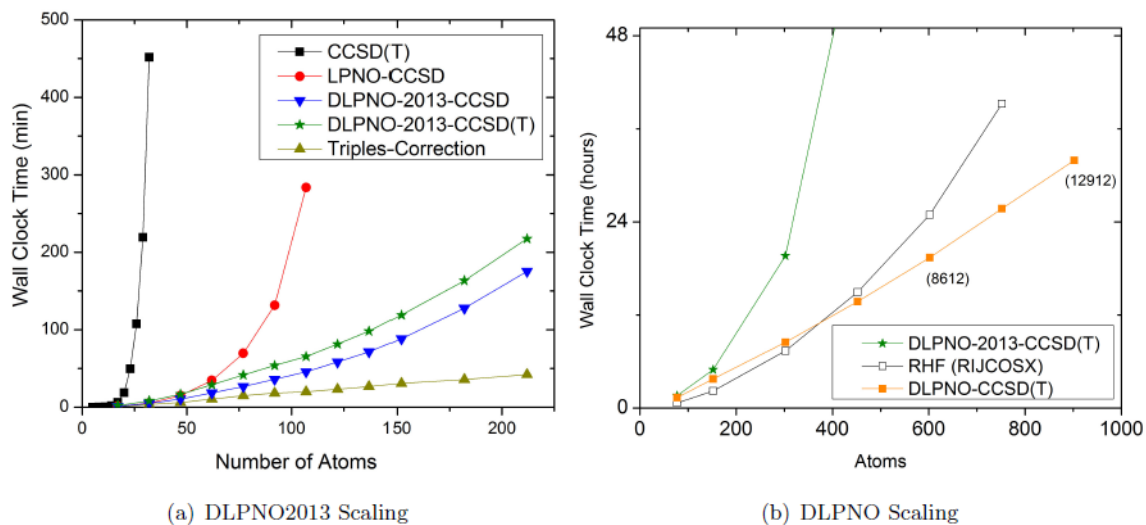
(a) DLPNO2013 Scaling
(b) DLPNO Scaling

Figure 8.5: a) Scaling behaviour of the canonical CCSD, LPNO-CCSD and DLPNO2013-CCSD(T) methods. It is obvious that only DLPNO2013-CCSD and DLPNO2013-CCSD(T) can be applied to large molecules. The advantages of DLPNO2013-CCSD over LPNO-CCSD do not show before the system has reached a size of about 60 atoms. b) Scaling behaviour of DLPNO2013-CCSD(T), DLPNO-CCSD(T) and RHF using RIJCOSX. It is obvious that only DLPNO-CCSD(T) can be applied to truly large molecules, is faster than the DLPNO2013 version, and even has a crossover with RHF at about 400 atoms.

## Multilevel methods

The systematic single method approach to solve the correlation problem is usually very time consuming (both human and computer time) so several multilevel extrapolation methods have been proposed. The multilevel methods are very complex looking but the main idea is to extrapolate both the correlation and basis. Below is the G2 and G3 multilevel methods. Note that Orca do not have the multilevel methods. It utilizes the F12-methods.

**Table 7.6** Steps in G2 and G3 theory for molecules[a,b]

| Step | G2 | G3 |
|---|---|---|
| (1) | HF/6-31G(d) geometry optimization | HF/6-31G(d) geometry optimization |
| (2) | ZPVE from HF/6-31G(d) frequencies | ZPVE from HF/6-31G(d) frequencies |
| (3) | MP2(full)/6-31G(d) geometry optimization (all subsequent calculations use this geometry) | MP2(full)/6-31G(d) geometry optimization (all subsequent calculations use this geometry) |
| (4) | $E[\text{MP4/6-311+G(d,p)}]$ $-E[\text{MP4/6-311G(d,p)}]$ | $E[\text{MP4/6-31+G(d)}] - E[\text{MP4/6-31G(d)}]$ |
| (5) | $E[\text{MP4/6-311G(2df,p)}]$ $-E[\text{MP4/6-311G(d,p)}]$ | $E[\text{MP4/6-31G(2df,p)}]$ $-E[\text{MP4/6-31G(d)}]$ |
| (6) | $E[\text{QCISD(T)/6-311G(d)}]$ $-E[\text{MP4/6-311G(d)}]$ | $E[\text{QCISD(T)/6-31G(d)}]$ $-E[\text{MP4/6-31G(d)}]$ |
| (7) | $E[\text{MP2/6-311+G(3df,2p)}]$ $-E[\text{MP2/6-311G(2df,p)}]$ $-E[\text{MP2/6-311+G(d,p)}]$ $+E[\text{MP2/6-311G(d,p)}]$ | $E[\text{MP2(full)/G3large}^{c}]$ $-E[\text{MP2/6-31G(2df,p)}]$ $-E[\text{MP2/6-31+G(d)}]$ $+E[\text{MP2/6-31G(d)}]$ |
| (8) | $-0.00481 \times$ (number of valence electron pairs) $-0.00019 \times$ (number of unpaired valence electrons) | $-0.006386 \times$ (number of valence electron pairs) $-0.002977 \times$ (number of unpaired valence electrons) |
| $E_0 =$ | $0.8929 \times (2) + E[\text{MP4/6-311G(d,p)}] +$ $(4) + (5) + (6) + (7) + (8)$ | $0.8929 \times (2) + E[\text{MP4/6-31G(d)}] +$ $(4) + (5) + (6) + (7) + (8)$ |

[a]For atoms, G3 energies are defined to include a spin-orbit correction taken either from experiment or other high-level calculations. In addition, different coefficients are used in step (8).
[b]In the G2 method, the 6-311G basis set and its derivatives are not defined for second-row atoms; instead, a basis set optimized by McLean and Chandler (1980) is used.
[c]Available at http://chemistry.anl.gov/compmat/g3theory.htm. Defined to use canonical 5 d and 7 f functions.

# F12-method

The multilevel methods are messy and they contain empirical parameters so a more systematic way is to extrapolate the correlation energy from smaller basis sets. The best extrapolation method for correlation energy at the moment is the F12-method. It clearly outperforms the old extrapolation methods. But nothing comes for free. The additional effort for the F12-MP2 calculation is rather high, a DZ F12 calculation is roughly as expensive as normal QZ calculation. This can be improve with RI-KJ methods.

```
#
# Correlation energies of the water molecule: extrapolation versus F12
#
# cc-pVDZ MP2: -0.201 380 894
```

```
# T :            -0.261 263 141
# Q :            -0.282 661 311
# T/Q :          -0.298 276 192  (normal extrapolation)
# Q/5 :          -0.300 598 282  (normal extrapolation)
# F12-DZ :       -0.295 775 804
# RI-F12-DZ :    -0.295 933 560 (cc-pVDZ/C note: basis for RI)
#                -0.295 774 489 (cc-pVTZ/C)
# F12-TZ :       -0.299 164 006
# RI-F12-TZ :    -0.299 163 478 (cc-pVQZ/C)
# F12-QZ :       -0.300 130 086
```

Note that F12-method is also available for CCSD(T). There the
F12 is much more efficient than the traditional extrapolation.


## Density Functional Theory


The traditional Quantum Chemical methods will approach
systematically the exact wave functions and thus the solution of
the correlation energy but this approach will lead to very heavy
computational procedures. The Density Functional Theory will
utilize another approach. In its hart is a proof that the ground
state of an electronic system depend only on the electron
density ρ(r).

$$\Psi(r_1, r_2, ..., r_N) \mapsto \Psi[\rho(r)]$$

This wave function is much much simpler than the true wf. The
problem is that we do not know the equations to solve the wf.
The basic ideas are form Kohn, Hohenberg and Sham (1963, 1964,
Kohn Nobel prize 1998).

The total energy is only a function of electron density $E^{tot}[\rho]$.
Unfortunately, we do not know accurate enough approximation to
this function (or functional). Kohn and Sham proposed that one
can solve effective non-interacting orbitals (φ) from HF-type
equations (the Kohn-Sham equations) with an effective potential
$V_{eff}$. Because these effective orbitals do not interact the single
Slater determinant is the exact wavefunction.

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(r)\right]\phi_n(r) = \epsilon_n\phi_n(r); \quad \rho(r) = \sum_n |\phi_n(r)|^2$$

Again, we do not know the K-S Hamiltonian or the effective potnetial, but it is useful to try to find a good approximation for it. Kohn and Sham showed that a simple model for the Exchange and Correlation (XC) energy will give good results. The formulation is quite similar to the HF:

$$\boldsymbol{FC} = \varepsilon\boldsymbol{SC}$$

$$F_{nm} = H_{nm} + J_{nm} - F_{nm}^{xc}$$

$$H_{nm} = \int \xi_n(r)\left[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon}\sum_I \frac{Z}{|r-R_I|}\right]\xi_m(r)\,d\tau$$

$$E^{XC} = \int f(\rho, \nabla\rho(r),..)d\tau; \quad F^{XC} = \frac{\delta E^{XC}}{\delta\rho(r)}$$

$$J = \frac{1}{2}\iint \frac{\rho(r_1)\rho(r_2)}{|r_1-r_2|}dr_1dr_2 \quad \rho(r) = \sum_{n,i} |c_{n,i}\xi_n(r)|^2$$

The difficult part is **the XC energy**. It is not known but several approximation are done. Formally the $E^{xc}$ can be written as

$$E^{xc}[\rho] = \langle T \rangle - T_s[\rho] + \langle W \rangle - J[\rho]$$

Where <T> is the exact kinetic energy, $T_s$ is the DFT K.E. <W> is the exact electron-electron interaction energy and J is the Coulomb energy of the electron density.

The is often expressed as an integral $E^{xc}[\rho] = \int \rho(r)\varepsilon_{xc}[\rho]dr$

The simplest Local Density Approximation (LDA) depend only on density, $E^{XC,LDA}[\rho(r)]$. The exchange part is easy ($\alpha = 1$)

$$\varepsilon_x[\rho] = -\frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\rho^{\frac{1}{3}}(r)$$

But the correlation is more complex. This functional can be obtained from **exact calculations** of homogenous electron gas (Ceperley-Alder 1980). There is also very simple Chachiyo

correlation functional ($a=\ln(2)-1)/2\pi^2$, b=20.456325..) which works
well.



The correlation energy density plot with the following legend and equations:

High electron density region                    Low electron density region

$r_s = (4\pi\rho/3)^{-1/3}$

● Ceperley-Alder 1980 Quantum Monte Carlo simulation

— Chachiyo 2016   $\varepsilon_c = a \ln\left(1 + \dfrac{b}{r_s} + \dfrac{b}{r_s^2}\right)$

— · — Perdew-Wang 1992 Fit Function

$$\varepsilon_c = -2A(1 + \alpha_1 r_s)\ln\left(1 + \frac{1}{2A\left(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^{p+1}\right)}\right)$$

- - - - Vosko-Wilk-Nusair 1980 Fit Function

$$\varepsilon_c = \frac{A}{2}\left\{\ln\frac{x}{X(x)} + \frac{2b}{Q}\operatorname{atan}\frac{Q}{2x+b} - \frac{bx_0}{X(x_0)}\left[\ln\frac{(x-x_0)^2}{X(x_0)} + \frac{2(b+2x_0)}{Q}\operatorname{atan}\frac{Q}{2x+b}\right]\right\}$$

$$x = \sqrt{r_s}, \quad X(x) = x^2 + bx + c, \quad Q = \sqrt{4c - b^2}$$

The LDA work reasonably well and it is a bit better than HF
(with few exceptions) but electrons are NOT homogenously spread
in molecules.  The next level is the **Generalized Gradient
Approximation**, $E^{XC,GGA}[\rho(r), \nabla\rho(r)]$. The GGA models are much better
but there is no simple (or even non-simple) procedure to build
the GGA functionals. For this reason there are a huge amount of
different GGA models.

One of the simplest ones that works is due to Axel Becke (1986),

$$E_x^{GGA} = \int E_{x,homog}(\rho) * f_x(\xi)d^3r, \quad \xi = \frac{(\nabla\rho)^2}{(2k_F\rho)^2}, \quad k_F = (3\pi^2\rho)^{1/3}, f_x^{B86}(\xi) = 1 + \frac{a\xi}{1+b\xi}$$

Where a and b are parameters, a=0.2351 and b=0.24308. 1988 Becke
proposed an improvement to this equation

$$f_x^{B88}(\xi) = 1 + \frac{a\xi}{1 + b\sqrt{\xi}\operatorname{arsh}(2(6\pi^2)^{1/3}\sqrt{\xi})}$$

Now a=0.2743 and b=9a/4π. This is very much used approximation for exchange energy.

There is a very extensive library of the XC functionals. The Libxc which is implemented to many codes (but not Orca, see the Orca manual)

http://www.tddft.org/programs/octopus/wiki/index.php/Libxc

The most common are BLYP and PBE. Even there are far too many GGA models, the DFT-GGA method have one very strong advantage. **It scales as $N^3$**. It is much more accurate than HF but it is much faster. With DFT we cannot get systematic improvement of the accuracy but it can be applied to big systems are the results are almost always good (same level as MP2).

One can also mix the HF and DFT theories. These are called **hybrid methods** and they are also very accurate. The most common of them is the B3LYP model also PBE0 model is good.

$$E_{xc}^{hyb} = aE_x^{HF} + (1-a)E_x^{GGA} + bE_c^{GGA}$$

For example PBE0, a=1/4, b=1. GGA=PBE;

$$E_{xc}^{hyb} = aE_x^{HF} + (1-a)E_x^{LDA} + b\,(E_x^{GGA} - E_x^{LDA}) + cE_c^{GGA} + (1-c)\,E_c^{LDA}$$

B3LYP is more complex: a=0.2, b=0.72, c=0.81.


The next GGA level is **meta-GGA** where the kinetic energy density is included to the GGA, $\tau(r) = 1/2 \sum_n |\nabla\varphi_n(r)|^2$

$$E^{XC,m\text{-}GGA}[\rho(r), \nabla\rho(r), \tau(r)].$$

Good meta-GGA's are TPSS (implemented to Orca), HCTC, M06L.

Last one can also combine MP2 and GGA. These are called **double hybrids**. In Orca B2PLYP is implemented.

One key defect of simple DFT method is the lack of dispersion interactions. There are included to the present HF either. On the other hand, quite accurate semi-empirical corrections can be used. The most used model is the Grimme D3 method. It is available for most of the GGA.

In Orca the usage is easy. (The D3BJ is Grimme version 3 corrections with Beck-Jonson damping model)


! PBE D3BJ TZVP opt …


As DFT cannot be improved systematically the results matters. The DFT wf's are variational but the models are not, so we cannot judge the quality of results with the correlation energy. The results can be compared to experiments or to more accurate quantum chemical methods.

Below there are few tables.

**TABLE 16.11**

## Homolytic Bond Dissociation Energies (kJ/mol)

| Bond Dissociation Reaction | Hartree-Fock | | B3LYP | MP2 | Experiment |
|---|---|---|---|---|---|
| | 3-21G | 6-31G* | 6-31G* | 6-31G* | |
| $CH_3-CH_3 \rightarrow CH_3\bullet + CH_3\bullet$ | 285 | 293 | 406 | 414 | 406 |
| $CH_3-NH_2 \rightarrow CH_3\bullet + NH_2\bullet$ | 247 | 243 | 372 | 385 | 389 |
| $CH_3-OH \rightarrow CH_3\bullet + OH\bullet$ | 222 | 247 | 402 | 410 | 410 |
| $CH_3-F \rightarrow CH_3\bullet + F\bullet$ | 247 | 289 | 473 | 473 | 477 |
| $NH_2-NH_2 \rightarrow NH_2\bullet + NH_2\bullet$ | 155 | 142 | 293 | 305 | 305 |
| $HO-OH \rightarrow OH\bullet + OH\bullet$ | 13 | 0 | 226 | 230 | 230 |
| $F-F \rightarrow F\bullet + F\bullet$ | −121 | −138 | 176 | 159 | 159 |
| Mean absolute error | 190 | 186 | 9 | 2 | — |

TABLE 16.17

## Absolute Activation Energies for Organic Reactions (kJ/mol)

| Reaction | Hartree-Fock | | B3LYP | MP2 | | Experiment |
|---|---|---|---|---|---|---|
| | 3-21G | 6-31G* | 6-31G* | 6-31G* | 6-311+G** | |
| $CH_3NC \longrightarrow CH_3CN$ | 238 | 192 | 172 | 180 | 172 | 159 |
| $HCO_2CH_2CH_3 \longrightarrow HCO_2H + C_2H_4$ | 259 | 293 | 222 | 251 | 234 | 167, 184 |
| (cyclohexadiene → benzene type) | 192 | 238 | 142 | 117 | 109 | 151 |
| (pyran ring rearrangement) | 176 | 205 | 121 | 109 | 105 | 130 |
| (cyclopentadiene + ethylene → norbornene) | 126 | 167 | 84 | 50 | 38 | 84 |
| (→ + $C_2H_4$) | 314 | 356 | 243 | 251 | 230 | — |
| $HCNO + C_2H_2 \longrightarrow$ (isoxazole) | 105 | 146 | 50 | 33 | 38 | — |
| (diene rearrangement) | 230 | 247 | 163 | 159 | 142 | — |
| (cyclobutene → butadiene) | 176 | 197 | 151 | 155 | 142 | — |
| (lactone → $+ CO_2$) | 247 | 251 | 167 | 184 | 172 | — |
| ($SO_2$ extrusion $+ SO_2$) | 205 | 205 | 92 | 105 | 92 | — |
| Mean absolute deviation from MP2/6-311+G** | 71 | 100 | 17 | 13 | — | — |

**Table 8.3** Mean and maximum absolute errors (kcal mol$^{-1}$) in enthalpies of activation and forward reaction for different methods

| Level of theory | Activation | | Reaction | |
|---|---|---|---|---|
| | Mean | Maximum | Mean | Maximum |
| **Reaction set 1[a,b]** | | | | |
| MNDO | 23.4 | 51.8 | 10.9 | 57.7 |
| AM1 | 9.3 | 34.2 | 7.5 | 22.1 |
| HF/6-31G(d)[c] | 13.6 | 30.6 | 10.5 | 24.8 |
| MP2 | 9.9 | 28.8 | 6.3 | 26.0 |
| BLYP | 5.9 | 21.9 | 5.9 | 13.0 |
| BLYP/6-311G(2df,2pd) | | | 5.8 | 16.0 |
| B3LYP | | | 5.0 | 9.4 |
| B3LYP/6-311G(2df,2pd) | | | 3.7 | 8.5 |
| B3PW91 | 3.7 | 12.9 | 6.8 | 17.7 |
| OLYP | | | 4.6 | 12.7 |
| OLYP/6-311G(2df,2pd) | | | 3.6 | 10.6 |
| O3LYP | | | 4.6 | 11.6 |
| O3LYP/6-311G(2df,2pd) | | | 2.8 | 7.1 |
| **Reaction set 2[d]** | | | | |
| HF | 12.4 | | 149.5 | |
| MP2 | 5.5 | | 24.4 | |
| QCISD | 3.9 | | 38.6 | |
| QCISD(T) | 3.1 | | 32.3 | |
| CBS-Q | 0.8 | | 1.3 | |
| MC-QCISD | 0.9 | | 1.1 | |
| MCG3 | 0.8 | | 0.8 | |
| BB95 | 8.3 | | 8.2 | |
| BLYP | 8.3 | | 6.8 | |
| BP86 | 9.4 | | 13.0 | |
| G96LYP | 6.9 | | 11.1 | |
| HCTH | 5.4 | | 5.3 | |
| mPWPW91 | 8.6 | | 7.2 | |
| OLYP | 6.0 | | 3.4 | |
| PBE | 9.5 | | 12.1 | |
| PWPW91 | 9.8 | | 12.1 | |
| VSXC | 5.1 | | 3.4 | |
| B1B95 | 3.7 | | 3.4 | |
| B97-1 | 4.2 | | 5.8 | |
| B97-2 | 3.1 | | 3.9 | |
| B98 | 4.1 | | 6.3 | |
| KMLYP | 2.9 | | 1.0 | |
| mPW1PW91 | 3.9 | | 8.0 | |
| MPW1K | 1.4 | | 14.9 | |
| PBE1PBE | 4.6 | | 7.1 | |
| B3LYP | 5.0 | | 7.2 | |

(*continued overleaf*)

They show that OLYP and B3LYP method is usually as good as MP2. Unfortunately the results depend a (quite) bit from the property we are looking but in most cases the DFT methods are as good as or better than MP2. There are much more tables in the Cramers book. Almost all methods the bond distances are quite good. For energies the HF or LDA are not reliable whereas most GGA's and correlated quantum chemistry methods are good. The reaction barriers are challenging form computational methods and in them the GGA methods work rather well.

Very crudely one can say that

Double hybrid < Meta-GGA ~ Hybrid < pure GGA << LDA

Naturally the GGA methods have some problems. The most obvious one is the difficulty to improve the XC-functionals. Another is the van der Waals interactions (or dispersion) which is important in **weakly bonded systems**. HF and by far most of the GGAs do not have them and they have to be added using additional (empirical) terms. In most cases the Grimme's D3 model works well. DFT have also problems to describe the hydrogen correctly. This is due to the **Self Interaction Error** (SIE). In DFT the density is the basic quantity and hydrogen sees its own density. This is not correct (think the Schrödinger equation of H atom). A good GGA will almost cancel this but not exactly. There are several Self Interaction Corrections (SIC) but they are difficult to use. Note that HF is exact for hydrogen so the hybrid functionals have smaller SIE and this is one reason of their success.

Like HF the DFT models do not give good HOMO-LUMO gap or absolute energy levels for electronic states.

Summary: It does not matter whether we like or dislike DFT, its **accuracy compared to computational cost is superior** to any of the traditional quantum chemistry methods. For large systems we need to use DFT until we get very efficient MP2-type methods.


In DFT the development is rather slow. Now there is quite a bit of interest of beyond-DFT methods. Like RPA, MP2 etc.

On the other hand, both these methods have enormous amount of applications covering almost all fields of chemistry. DFT can be used to model single molecules, clusters of atoms, surfaces, solid systems and liquids. Systems up to 100.000 valence electrons can be computed. An emerging research field is quantum mechanical materials screening where properties of materials (or molecules) will be evaluated computationally and this information is used to help the synthetic work.

## Linear scaling DFT calculations

The long term dream of quantum chemistry is to have a linear scaling (or N log N) code. There are many codes that claim to have achieve this, like ALMO in CP2K, BigDFT or CONQUEST. Some of them are not effective for real 3D systems, some of them are quite unstable (ALMO) but this is really the direction to go. Typically, they have complex data initialization and they are efficient only for large systems. So far, I have not done any research project with linear scaling codes.

CONQUEST is a large scale DFT electronic structure code, capable of both diagonalisation and linear scaling, or O(N), calculations. It has been developed jointly by NIMS (National Institute for Materials Science, Japan) and UCL. The code is designed to perform DFT calculations on very large systems (containing tens of thousands, hundreds of thousands or even millions of atoms). It can be run at different levels of precision, ranging from *ab initio* tight binding up to full DFT with plane wave accuracy. It is capable of operation on a range of platforms from workstations up to high performance computing centres. These web pages contain information on the code, and its applications, as well as separate areas for developers.
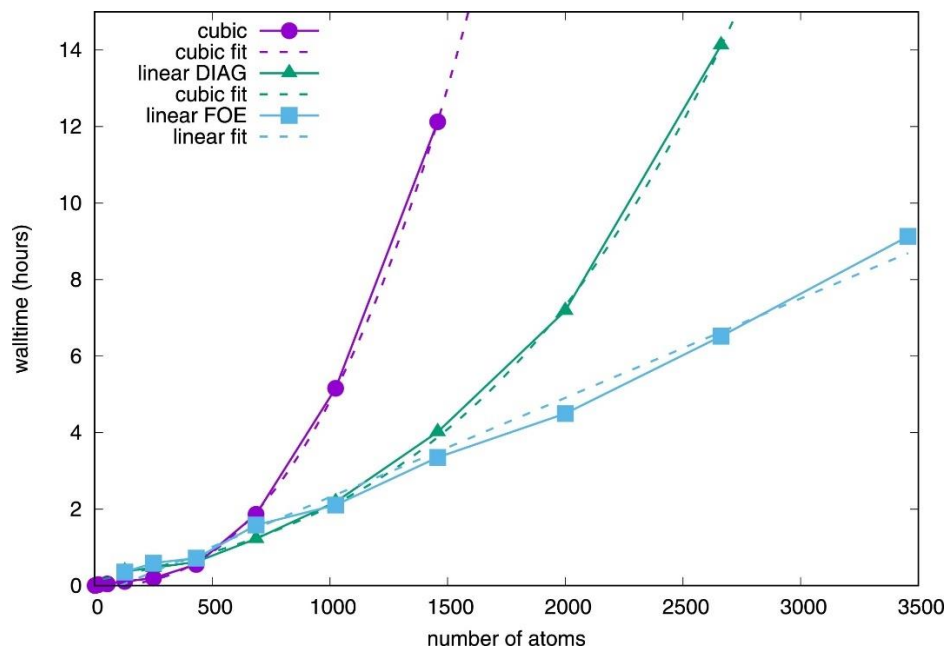
From.  Mohr et al. Nuclear Materials and Energy 15, Pages 64-70

Practical quantum chemistry calculations

**The first choice is the DFT with modern GGA or hybrid method.**
The basis should be TZ level. If possible test calculations
(very often single point calculations are enough) with MP2 at
least TZ basis should be done. The state-of-the-art basis set
extrapolation methods like F12-RI-MP2 are efficient to estimate
the infinite basis set limit. CCSD calculations are usually too
expensive, but the DLPNO-CCSD(T) method is very promising. If the
DLPNO-CCSD(T) method is available use it but *warning* it takes a lot
of memory.