The story so far

- The Hartree wavefunction is based on molecular orbitals:

$$\Psi_{\mathrm{H}}(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$$

  and models E_{T}, E_{V} and E_{J}, but is not antisymmetric.

- The Hartree-Fock wavefunction is antisymmetric and can therefore model the exchange energy, E_{K}

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

- Hartree-Fock theory has an intrinsic error. We call this the correlation energy and is defined by:

$$E_{\mathrm{C}} = E - E_{\mathrm{HF}}$$

Energy decomposition

- The electronic Hamiltonian (energy operator) has several terms:

$$\hat{H}_e = \hat{T}_e(\mathbf{r}) + \hat{V}_{ne}(\mathbf{r}; \mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

- This operator is linear, thus the electronic energy can also be written as a sum of several terms:

$$E_e = \underbrace{E_T + E_V}_{\hat{T}_e + \hat{V}_{ne}} + \underbrace{E_J + E_K + E_C}_{\hat{V}_{ee}}$$

- The electron-electron repulsion term has been broken into three terms: $E_J + E_K + E_C$

Electronic energy decomposition

- E_J is the coulomb repulsion energy.
  This energy arises from the classical electrostatic repulsion between the charge clouds of the electrons and is correctly accounted for in the Hartree wavefunction.

- E_K is the exchange energy.
  This energy directly arises from making the wavefunction antisymmetric with respect to the interchange of electronic coordinates, and is correctly accounted for in the Hartree-Fock wavefunction.

- E_C is the correlation energy.
  This is the error associated with the mean-field approximation which neglects the instantaneous interactions of the electrons. So far we do not have wavefunction which models this part of the energy.

Electronic energy decomposition

The total electronic energy can be decomposed as follows:

$$E = E_T + E_V + E_J + E_K + E_C$$

- For the Ne atom, the above energy terms are:

$$
\begin{aligned}
E_T &= +129 \ E_h \\
E_V &= -312 \ E_h \\
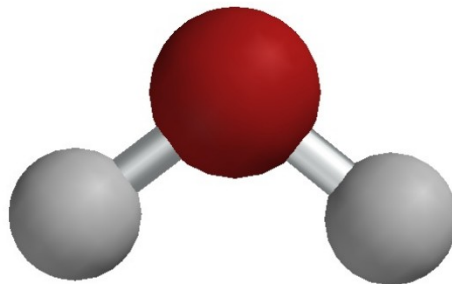E_J &= +66 \ E_h \\
E_K &= -12 \ E_h \quad 9.3\% \\
E_C &= -0.4 \ E_h \quad 0.3\%
\end{aligned}
$$

- The HF energy accounts for more than 99% of the energy
- If the correlation energy is so small, can we neglect it?

Consider the atomisation energy of the water molecule:

Energy	H_2O	2 H + O	ΔE
E_{HF}	-76.057770	-75.811376	0.246393
E_{CCSD}	-76.337522	-75.981555	0.355967

If we neglect the correlation energy in the atomisation of water we make a 30% error!

The electron correlation energy

- The correlation energy is sensitive to changes in the number of electron pairs.
- The correlation energy is always negative.
- There are two components to the correlation energy:
  - Dynamic correlation is the energy associated with the dance of the electrons as they try to avoid one another. This is important in bond breaking processes.
  - Static correlation arises from deficiencies in the single determinant wavefunction and is important in systems with stretched bonds and low-lying excited states.
- Electron correlation gives rise to the inter-electronic cusp.
- Computing the correlation energy is the single most important problem in quantum chemistry.

Modeling the correlation energy

There exists a plethora of methods to compute the correlation energy, each with their own strengths and weaknesses:

- Configuration interaction (CISD, CISD(T))
- Møller-Plesset perturbation theory (MP2, MP3...)
- Quadratic configuration interaction (QCISD)
- Coupled-cluster theory (CCD, CCSD, CCSDT)
- Multi-configuration self-consistent field theory (MCSCF)
- Density functional theory (DFT)

In practice, none of these methods are exact, but they all (except for DFT) provide a well-defined route to exactitude.

- Recall the HF wavefunction is a single determinant made up of the product of occupied molecular orbitals ψ_i:

$$\Psi_0 = |\psi_1, \psi_2, \ldots \psi_N\rangle$$

$$\psi_i = \sum_\mu c_{\mu i} \chi_\mu$$

- This is referred to as a single configuration treatment.
- If we have M atomic orbitals, the HF method gives us M molecular orbitals, but only the lowest N are occupied.
- The remaining $M - N$ orbitals are called virtual orbitals.

Configuration interaction

- We can create different configurations by "exciting" one or more electrons from occupied to virtual orbitals:

$$
\begin{aligned}
\Psi_0 &= |\psi_1, \psi_2, \ldots \psi_i, \psi_j, \ldots \psi_N\rangle \\
\Psi_i^a &= |\psi_1, \psi_2, \ldots \psi_a, \psi_j, \ldots \psi_N\rangle \\
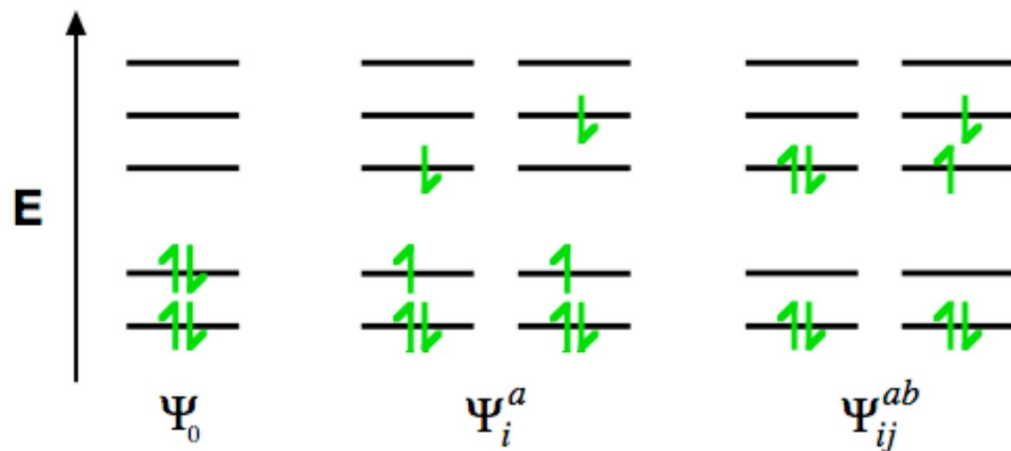\Psi_{ij}^{ab} &= |\psi_1, \psi_2, \ldots \psi_a, \psi_b, \ldots \psi_N\rangle
\end{aligned}
$$

- These configurations can be mixed together to obtain a better approximation to the wavefunction:

$$
\Psi_{\mathrm{CI}} = c_0 \Psi_0 + \sum_i c_i^a \Psi_i^a + \sum_{ij} c_{ij}^{ab} \Psi_{ij}^{ab} + \ldots
$$

- The CI coefficients, $c_i^a, c_{ij}^{ab} \ldots$ can be found via the variational theorem.

Configurations

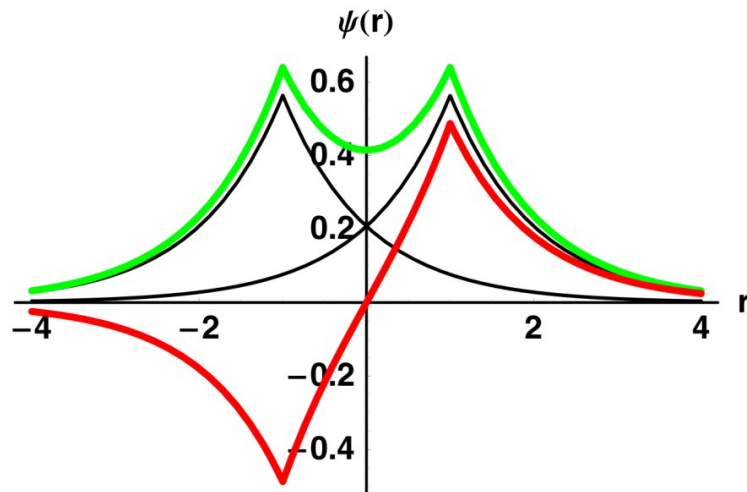- To improve on the HF wavefunction, we need to consider excited configurations:

- These configurations can be mixed to give a better approximation to the wavefunction :

$$\Psi_{CI} = c_0 \Psi_0 + \sum_i c_i^a \psi_i^a + \sum_{ij} c_{ij}^{ab} \psi_{ij}^{ab} + \dots$$

How does this help?

Consider a minimal H_2 system with two MOs:

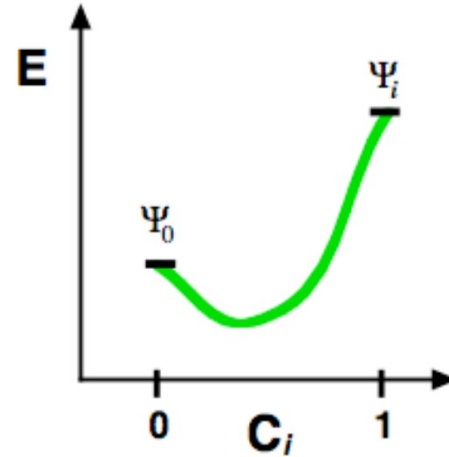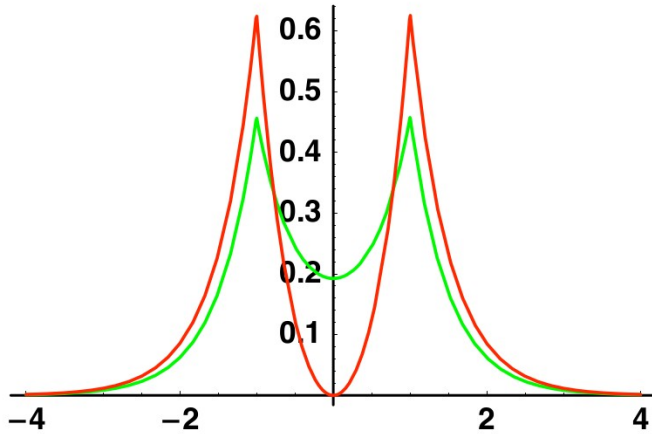$$\psi_1 = \sigma = \frac{1}{\sqrt{2}} \left(\chi_{1s}^A + \chi_{1s}^B \right)$$

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

$$\Psi_{CI} = C_0 \; \underline{\underline{\text{\textuparrow\textdownarrow}}} \; + C_1 \; \underline{\underline{\text{\textuparrow}}} \; + C_2 \; \underline{\underline{\text{\textdownarrow}}} \; + C_3 \; \underline{\underline{\text{\textuparrow\textdownarrow}}}$$

The node in the σ^* orbital allows the electrons to spend more time apart, thus lowering the electron repulsion energy.

Orbital densities

The picture can be made clearer by considering density plots of the two orbitals:

$$\Psi_{CI} = C_0 \;\underline{\underline{\uparrow\downarrow}}\; + \; C_1 \;\underline{\underline{\uparrow}}\; + \; C_2 \;\underline{\underline{\downarrow}}\; + \; C_3 \;\underline{\underline{\uparrow\downarrow}}$$

- This mixing is a compromise as E_T and E_V also change.
- This can be viewed as a dynamic correlation effect.

How does this help?

- Adding in configurations also helps modelling stretched bonds.

$$C_0 \approx 1 \qquad\qquad C_0 \approx 0$$
$$C_1 \approx 0 \qquad\qquad C_1 \approx 1$$

- This can be viewed as a static correlation effect.

Configuration interaction

- If we allow all possible configurations to mix in then we obtain the Full-CI wavefunction. This is the most complete treatment possible for a given set of basis functions.
- Complete-CI is Full-CI in an infinite basis set and yields the exact non-relativistic energy.
- The cost of full-CI scales exponentially and is therefore only feasible for molecules with around 12 electrons and modest basis sets.
- Truncated CI methods limit the types of excitations:
  - CIS adds only single excitations (same as HF!)
  - CID adds only double excitations
  - CISD adds single and double excitations, $\mathcal{O}(N^6)$
  - CISDT adds single, double and triple excitations, $\mathcal{O}(N^8)$

Size consistency

- A method is size-consistent if it yields M times the energy of a single monomer when applied to M non-interacting monomers.

- HF and Full-CI theories are size consistent, but truncated CI approaches are not.

- A method that is not size-consistent:
  - Yields poor dissociation energies.
  - Treats large systems poorly.

- Coupled-cluster wavefunctions are like CI wavefunctions, but include terms to maintain size-consistency.
  - CCSD includes all single and double excitations, but also includes some quadruple excitations.

- Coupled-cluster wavefunctions are not variational.

Size consistency

- The CISD wavefunctions for two separate two-electron systems includes double excitations on both:
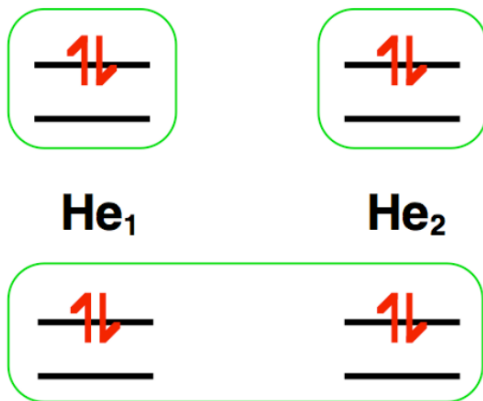
- When considered as a single system, however, these lead to quadruple excitations, which are not included in CISD.
- CCSD includes these types of excitation, making it size-consistent.

Møller-Plesset perturbation theory

- In Møller-Plesset Perturbation Theory the Hamiltonian is divided into two parts:

$$\hat{H} = \hat{H}_0 + \lambda\hat{V}$$

- $\hat{H}_0$ is the Hartree-Fock hamiltonian.
- $\lambda\hat{V}$ is a perturbation, which is assumed to be small.
- The wavefunction and energy are then expanded as a power series in λ (which is later set to 1):

$$\Psi_\lambda = \Psi_0 + \lambda\Psi_1 + \lambda^2\Psi_2 + \ldots$$

$$E_\lambda = E_0 + \lambda E_1 + \lambda^2 E_2 + \ldots$$

- Ψ_0 and E_0 are the HF wavefunction and energy.

Møller-Plesset perturbation theory

- MPn is obtained by truncating the expansion at order λ^n.
- The MP1 energy is the same as the HF energy.
- The MP2 energy is given by:

$$E_{\mathrm{MP2}} = \sum_{i<j}^{\mathrm{occ}} \sum_{a<b}^{\mathrm{vir}} \frac{|\langle \Psi_0 | \hat{V} | \Psi_{ij}^{ab} \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

- The cost of calculating the MP2 energy scales as $\mathcal{O}(N^5)$ and typically recovers $\sim$80-90% of the correlation energy.
- The MPn energy is size-consistent but not variational.
- The MP series may diverge for large orders.

Scaling

The number of basis functions N can be used as a measure of the size of the system. The cost of different methods scales differently:
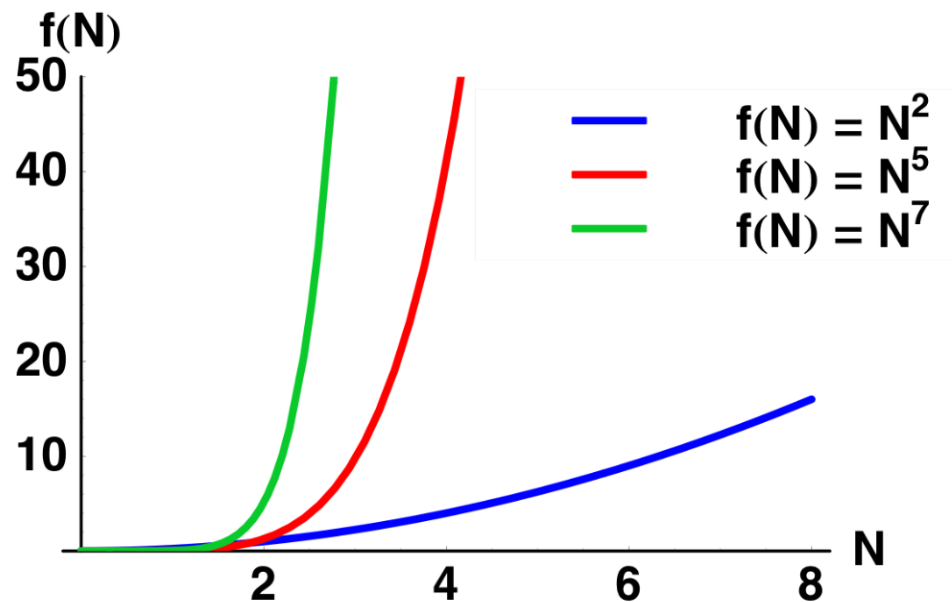
- HF formally scales as $\mathcal{O}(N^4)$, practically as $\mathcal{O}(N^2)$
- MPn scales as $\mathcal{O}(N^{n+3})$
- CCSD and CISD are $\mathcal{O}(N^6)$
- CCSD(T) scales as $\mathcal{O}(N^7)$
- CCSDT scales as $\mathcal{O}(N^8)$
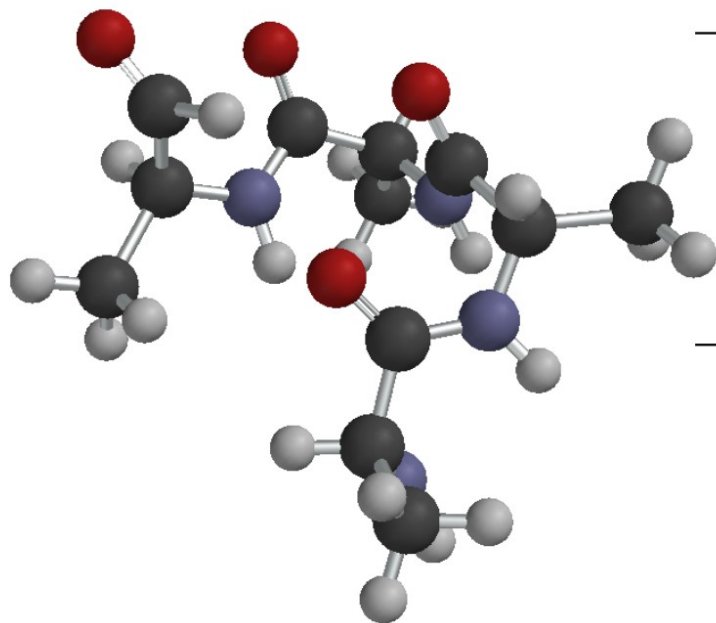
System	t_{HF}	t_{MP2}	t_{CCSD}
Ala$_1$	2.6 s	40 s	58 m
Ala$_2$	47 s	7 m	
Ala$_3$	200 s	31 m	
Ala$_4$	8 m		

Summary of post-HF methods

- Correlated wavefunction methods:

Theory	Finite Expansion	Variational	Size-Consistent
CI	✔	✔	✘
CC	✔	✘	✔
MP	✘	✘	✔

- Each of these methods gives a hierarchy to exactitude.
- Full-CI gives the exact energy (within the given basis set).
- The concepts of variational and size-consistent methods.
- Coupled-cluster methods are currently the most accurate generally applicable methods in quantum chemistry.
- CCSD(T) has been called the "gold standard" and is capable of yielding chemical accuracy (< 1 kcal/mol error).

What is the density?

- The electron density is a fundamental quantity in quantum chemistry:

$$\rho(\mathbf{r}_1) = N \int \cdots \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)d\mathbf{r}_2 \ldots d\mathbf{r}_N$$

- $\rho(\mathbf{r})d\mathbf{r}$ gives a measure of the probability of finding an electron in the volume element $d\mathbf{r}$.
- It is a function of three variables (x, y, z) and is therefore (relatively) easy to visualise.

What is a functional?

- A function takes a number and returns another number:
$$f(x) = x^2 - 1 \qquad f(3) = 8$$

- An operator takes a function and returns another function:
$$\hat{D}(f) = \frac{df}{dx} \qquad \hat{D}(x^2 - 1) = 2x$$

- A functional takes a function and returns a number:
$$F[f] = \int_0^1 f(x)\,dx \qquad F[x^2 - 1] = -2/3$$

What is a density functional?

- A density functional takes the electron density and returns a number, for example:

$$N[\rho] = \int \rho(\mathbf{r})d\mathbf{r}$$

  simply gives the number of electrons in the molecule.
- Density functional theory (DFT) focusses on functionals that return the energy of the system.

What is a density functional?

The total energy can be decomposed into the following parts:

$$E = E_{\text{T}} + E_{\text{V}} + E_{\text{J}} + E_{\text{K}} + E_{\text{C}}$$

- The classical potential energy terms of the total energy can be expressed exactly in terms of the density:

$$E_{\text{J}} = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$E_{\text{V}} = -\sum_A \int \frac{Z_A \rho(\mathbf{r})}{|\mathbf{R}_A - \mathbf{r}|} d\mathbf{r}$$

- What about E_{T}, E_{K} and E_{C}?

Orbital functionals

- In Hartree-Fock theory, E_T, E_K and E_C, are all orbital functionals, eg:

$$E_T = -\frac{1}{2} \sum_i \int \psi_i(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) d\mathbf{r}$$

- No (known) exact expression for the kinetic energy in terms of ρ exists.

- The exchange energy is non-classical, so should we expect there to be an expression for the exchange energy in terms of the classical density?

The Hohenberg-Kohn theorems

The First Hohenberg-Kohn Theorem

The electron density ρ determines the external potential ν.

- This theorem shows a one-to-one correspondence between ρ and ν and therefore (via the S.W.E.) Ψ.
- It also shows that there exists a universal and unique energy functional of the density.

The Second Hohenberg-Kohn Theorem

- For any valid trial density, $\tilde{\rho}$: $\quad E_\nu \leq E_\nu[\tilde{\rho}]$

- The second HK theorem establishes a variational principle for ground-state DFT.

Density functional theory

- The HK theorems are non-constructive, so we don't know what the form of the universal functional is.
- Research in DFT largely focusses on the development of approximate functionals that model experimental data.
- Kinetic energy functionals are particularly problematic as E_T is so large and even a small relative error gives large absolute errors.
- Almost all DFT calculations rely on the Kohn-Sham approximation, which avoids the need for a kinetic energy density functional.
- Different DFT methods differ in the way they represent E_X and E_C.

The uniform electron gas

- The uniform electron gas is a model system with a constant density of electrons.

- In 1930 Dirac showed that the exact exchange energy for this system is given by:

$$E_X = -C_x \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}$$

- Much later, Vosko, Wilk and Nusair parameterised a correlation functional (VWN) based on the UEG, its form is more complicated and it is inexact.

Local density approximation

- Applying the UEG functionals to molecular system is called the local (spin) density approximation (LDA).
- Combining the Dirac and VWN expressions gives the S-VWN functional.
- The LDA functional for E_X underestimates the true exchange energy by about 10% whereas the VWN functional overestimates E_C by as much as 100%.
- Together they overbind molecular systems.
- The constant C_X is sometimes scaled to account for the over-binding, this gives X_α theory.

Gradient corrected functionals

- Gradient corrected functions depend on $\nabla\rho$ as well as ρ.
- The gradient helps to account for deviations from uniformity in molecular systems.
- The generalised gradient approximation exchange functionals have the form

$$E_X = \int \rho^{4/3}(\mathbf{r})g(x)d\mathbf{r}$$

  where x is the reduced gradient.
- Different GGAs, such as Perdew '86 and Becke '88 are defined by different $g(x)$ functions.

GGA correlation functionals

- There are also GGA correlation functionals such as Lee-Yang-Parr (LYP) and Perdew '86.

- E_X and E_C can be mixed and matched, although certain combinations such as BLYP work particularly well.

- Combining a correlation functional with Hartree-Fock exchange does not work well, but hybrid functionals do:

$$E^{\mathrm{B3LYP}} = (1-c_1)E_X^{\mathrm{D30}} + c_1 E_K^{\mathrm{Fock}} + c_2 E_X^{\mathrm{B88}} + (1-c_3)E_C^{\mathrm{VWN}} + c_3 E_C^{\mathrm{LYP}}$$

- B3LYP is *the* most popular density functional that is used and yields very good structural and thermochemical properties.

Strengths and weaknesses

Advantages of DFT methods include:

- Low computational cost
- Good accuracy for structures and thermochemistry
- The density is conceptually simpler than Ψ

Disadvantages of DFT methods include:

- Can fail spectacularly and unexpectedly
- No systematic way of improving the results
- Integrals require numerical quadrature grids

Summary

- A functional takes in a function and returns a number.
- The density, $\rho(\mathbf{r})$, contains all the information necessary, as shown by the Hohneberg-Kohn theorems.
- Density functionals can be used to compute the difficult exchange and correlation energies cheaply.
- LDA functionals, *e.g.* S-VWN, are based on the UEG, they overbind.
- GGA functionals, *e.g.* B-LYP, incorporate the reduced density gradient and are much more accurate.
- Hybrid functionals, *e.g.* B3LYP, incorporate Fock exchange and are the most accurate.

The Pople Diagram

- A minimal basis Hartree-Fock calculation forms our baseline, other levels of theory distinguish themselves by their treatment of the correlation energy (left to right) and the size of the basis (top to bottom)

	HF	MP2	MP3	MP4	CCSD(T)	···	Full CI
Minimal	Low-level	···		···		···	Unbalanced
Split-Valence	···	···					
Polarised							
Diffuse	···						
Polarised + Diffuse							
⋮						⋱	
Infinite	Unbalanced	···					Exact!

Establishing the reliability of a method

- Experimental data forms a valuable means of establishing the reliability of a particular level of theory.

- Data sets such as the G2 and G3 sets are made up of accurate values with experimental uncertainties of less than 1 kcal/mol (chemical accuracy).

- The G2 set consists of thermochemical data including atomisation energies, ionisation potentials, electron affinities and proton affinities for a range of small molecules.

- These data set can be used to benchmark a level of theory.

- What if we want to apply our method to an unknown system?

Establishing the reliability of a method

- If we wish to apply a level of theory to a system that has no experimental data available, we need to converge the level of theory to have confidence in our results.

- We start near the top left-hand (cheap) corner of the Pople diagram and move along the diagonal towards the bottom right-hand (expensive) corner carrying out several calculations.

- When we see no significant improvement in the result, then we conclude that we have the correct answer.

- Note that we cannot apply this approach to DFT methods (although we can converge the basis set)

Specifying the level of theory

- Geometric properties converge faster (with respect to the level of theory) than the energy (they are less sensitive to correlation)
- It is common to optimise the geometry at a low-level of theory, and then compute the energy at a higher level of theory
- The notation for this is:
  energy-method / basis-set // geometry-method / basis-set
- The // can be read as 'optimised at'.
- For example:
  CCSD(T) / 6-311G(2d,p) // HF / 6-31G

Performance

Average deviation from experiment for bond-lengths of 108 main-group molecules using 6-31G(d,p)

Bond-length	HF	MP2	LDA	GGA	Hybrid
Deviation Å	0.021	0.014	0.016	0.017	0.011

Average deviation from experiment for atomisation energies of 108 main-group molecules using 6-31G(d,p)

AE	HF	MP2	LDA	GGA	Hybrid
Deviation kcal/mol	119.2	22.0	52.2	7.0	6.8

Calculated electron affinity (eV) for Fluorine:

$$F + e^- \rightarrow F^-$$
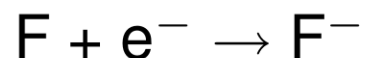
	HF	MP2	B3LYP
STO-3G	-10.16	-10.16	-9.01
3-21G	-1.98	-1.22	-0.86
6-31G(d)	-0.39	+1.07	+1.05
6-311+G($2df,p$)	+1.20	+3.44	+3.46
6-311+G($3df,2p$)	+1.19	+3.54	+3.46
Experiment		+3.48	

Performance

Convergence of MP methods relative to Full-CI using the STO-3G basis.

Method	HCN	CN$^-$	CN
MP2	-91.82033	-91.07143	-91.11411
MP3	-91.82242	-91.06862	-91.12203
MP4	-91.82846	-91.07603	-91.13538
MP5	-91.83129	-91.07539	-91.14221
MP6	-91.83233	-91.07694	-91.14855
MP7	-91.83264	-91.07678	-91.15276
MP8	-91.83289	-91.07699	-91.15666
Full-CI	-91.83317	-91.07706	-91.17006
$\Delta E < 0.001$	MP6	MP6	MP19

- In general, the use of moderately large basis sets such as 6-311G(d,p) combined with the MP2 treatment of electron correlation leads to calculated structures very close to experiment.
- For difficult systems, the Coupled Cluster (CC) methods correspond to an electron correlation treatment better than MP4 and thus greater accuracy is achieved, e.g. ozone:

Parameter	MP2	CCSD	CCSD(T)	Expt
O–O bond (Å)	1.307	1.311	1.298	1.272
$\angle$OOO (°)	113.2	114.6	116.7	116.8