

Methods

The Coulomb Integral

The quantum mechanical nature of the electron means that we cannot describe its location in space very well. So instead of giving a point charge q_1 for the electron, which is quantum mechanical and doesn't behave like a "point" at all, we use a "density". The total amount of charge is still one (in atomic units, e in reality); it is just smeared out a little, **Figure 1**. This is really a *probability density distribution* (see appendix one for an idea of how to think about this), ie if we went to a position r_1 we would find an electron a there about $\rho_a(r_1)$ of time. We often we drop the words "probability" and "distribution" and just say that ρ is the electron density. We determine the density from the wavefunction squared $\rho_a(r) = \psi_i^*(r)\psi_i(r)$.

If we had two electrons they would interact via the Coulomb electron-electron interaction potential J_{ee} .

$$J_{ee} = \sum_{a,b}^{N_e} \frac{q_a q_b}{r_{ij}}$$

However, we need to account for the electrons "spreading out". On average the amount of charge seen at point r_1 is $\rho(r_1)$, and this will interact with another small portion of charge, for example $\rho_b(r_2)$ (belonging to electron b at position r_2 on the diagram), **Figure 2**. Notice that the distance to and the size of the bits of charge $\rho_b(r_i)$ change slightly for each bit of charge. We need to sum over all these interactions, or rather we need to integrate because the distribution is a continuous one. To simplify the equation I am using r' to count all the possible positions under distribution b :

$$J_{ee} \Rightarrow \frac{\rho_a(r_1) \int \rho_b(r') dr'}{|r_1 - r'|}$$

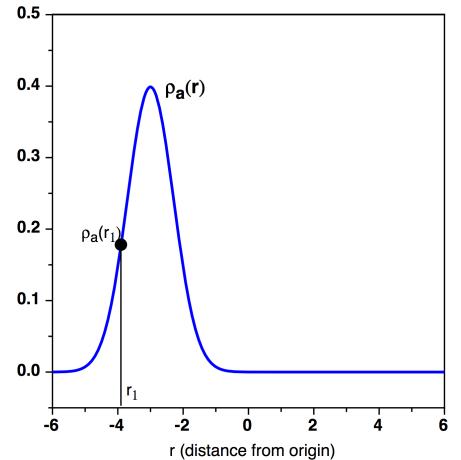


Figure 1 Quantum mechanical electron

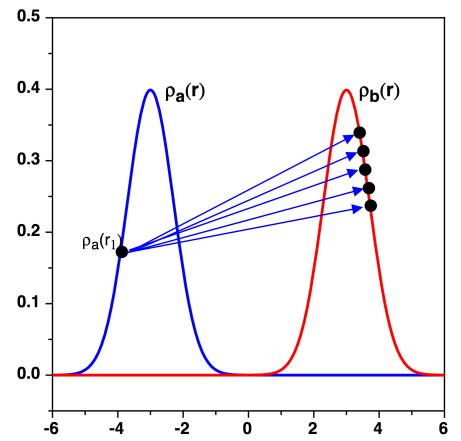


Figure 2 Interacting electrons

Then we need to sum (or rather integrate) over all the small portions of charge on ρ_a , **Figure 3**.

$$J_{ee} \Rightarrow \frac{\int \rho_a(r) dr \int \rho_b(r') dr'}{|r_1 - r'|}$$

So far we have included only electrons a and b , we also need to count the interaction of every electron with every other electron, so the final equation is:

$$J_{ee} = \frac{1}{2} \sum_{a,b}^{N_e} \frac{\int \rho_a(r) dr \int \rho_b(r') dr'}{|r - r'|}$$

If you think about this carefully you will realise that all the interactions will be counted twice, the interaction of $\rho_a(r)$ with $\rho_b(r')$ and then the interaction of $\rho_b(r')$ with $\rho_a(r)$, and so we add the factor of 1/2 in front to remove the double counting.

You might have noticed that it is now possible for an electron to interact with itself! Part of the distribution at say $\rho_a(r_1)$ could interact with another part of the same distribution at $\rho_a(r_3)$. If you ever study density functional theory in detail this "self interaction" becomes quite an issue. More detail on this is provided shortly.

Lets go back to considering only two interacting electron clouds:

$$J_{ab} = \iint \rho_a(e_1) \frac{1}{r_{12}} \rho_b(e_2) dr_1 dr_2$$

The Coulomb potential represents the potential that an electron distributed over $\rho_b(e_2)$ experiences due to the charge distribution $\rho_a(e_1)$ of another electron. Thus the interaction between charges located at x_1 and x_2 is moderated by the amount of charge at these points (or really the probability of an electron being at that position).

J_{ab} is what physicists call a "*local*" potential, it can be written in the following form

$$\begin{aligned} J_{ab} &= \iint \rho_a(e_1) \frac{1}{r_{12}} \rho_b(e_2) dr_1 dr_2 \\ &= \int \hat{J}(e_2) \rho_b(e_2) dr_2 \quad \hat{J}(e_2) = \int \rho_a(e_1) \frac{1}{r_{12}} dr_1 \end{aligned}$$

When written this way there is only one important orbital for the *Coulomb operator* $\hat{J}(e_2)$, in this case $\psi_a(e_1)$. The electron density of electron 1 $\rho_a(e_1)$ is the product of an orbital with its complex conjugate; $\rho_a(r) = \psi_a^*(r)\psi_a(r)$. We can substitute this into the Coulomb integral equation and obtain:

$$J_{ab} = \iint \psi_a^*(e_1) \psi_a(e_1) \frac{1}{r_{12}} \psi_b^*(e_2) \psi_b(e_2) dr_1 dr_2$$

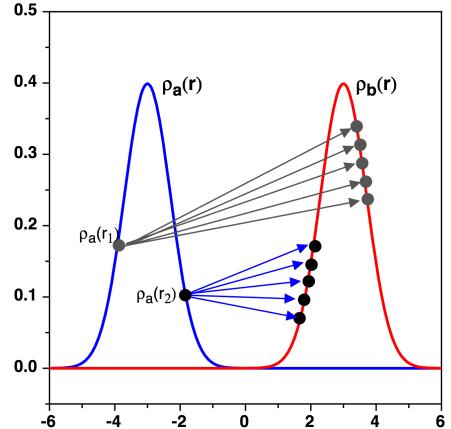


Figure 3 Integrate over first electron

The Exchange Integral

However, because electrons are indistinguishable, we must be able to swap electron labels around with no effect on the expression other than each swap introducing a negative sign. If I swap just two of the electron labels in a Coulomb integral, I have what is called the *Exchange integral*:

$$K_{ab} = - \int \int \psi_a^*(e_1) \psi_a(e_2) \frac{1}{r_{12}} \psi_b^*(e_2) \psi_b(e_1) dr_1 dr_2$$

\uparrow \uparrow

Now we have a problem; we cannot write the equation in terms of electron densities $\rho(r)$! $\rho(e_1) = \int \psi_a^*(e_1) \psi_a(e_1) dr_1 \neq \int \psi_a^*(e_1) \psi_a(e_2) dr_1$

K_{ab} is what physicists call a "*non-local*" potential, $\hat{K}(e_2)$ is the *Exchange operator* and cannot be written in terms of densities and has to be written such that it depends on the value of two orbital parameters $\psi_a^*(e_1)$ and $\psi_b(e_1)$.

$$\begin{aligned} K_{ab} &= - \int \psi_b^*(e_2) \left[\int \psi_a^*(e_1) \frac{1}{r_{12}} \psi_b(e_1) dr_1 \right] \psi_a(e_2) dr_2 \\ &= \int \psi_b^*(e_2) \hat{K}(e_2) \psi_a(e_2) dr_2 \quad \hat{K}(e_2) = \int \psi_a^*(e_1) \frac{1}{r_{12}} \psi_b(e_1) dr_1 \end{aligned}$$

Not only does the Coulomb potential have nasty decay properties, but the Exchange potential being non-local makes things seriously difficult computationally.

This also means that we cannot simply write the quantum mechanical component of V_{ee} as $V_{ee} = J_{ee} + K_{ee}$ where K_{ee} is the quantum mechanical component. We cannot represent K_{ee} in terms of densities. Now we are left with two components of the electron-electron interaction potential written in terms of integrals J_{ab} and K_{ab} . We can present both potentials in terms of the orbital components, and re-write these grouping the parts belonging to e_2 in the center:

$$\begin{aligned} K_{ab} &= - \int \psi_b^*(e_2) \left[\int \psi_a^*(e_1) \frac{1}{r_{12}} \psi_b(e_1) dr_1 \right] \psi_a(e_2) dr_2 \\ J_{ab} &= \int \psi_b^*(e_2) \left[\int \psi_a^*(e_1) \frac{1}{r_{12}} \psi_a(e_1) dr_1 \right] \psi_b(e_2) dr_2 \end{aligned}$$

The parts in the square brackets are the operators just introduced, these are operators because they act on wavefunctions.

We cannot write the Schrödinger equation as we would like (ie in terms of densities) because of the exchange term, however, we can write the "Schrödinger equation" as a orbital equation, which we call the *Hartree-Fock (HF) equation*:

$$\begin{aligned} H_e &= T_e + V_{ne} + V_{ee} \\ \left[\frac{-1}{2} \nabla^2(e_1) - \sum_{\alpha} \frac{Z_{\alpha}}{r_1 - R_{\alpha}} + \frac{1}{2} \sum_{a,b} [J_b(e_1) - K_b(e_1)] \right] \psi_a(e_1) &= \epsilon_a \psi_a(e_1) \end{aligned}$$

The first term is the kinetic energy, the second term is the attractive nuclear-electron potential and the third term arises out of the electron-electron interaction potential (cf Lecture 1). Of course I've skipped over some details and tried to keep things as simple as possible in arriving at this equation.

Basic DFT

Just above HF in the hierarchy of methods are those labelled DFT, DFT stands for *Density Functional Theory*. DFT theory grew out of the solid state physics community and hence starts from a different perspective compared to HF theory. A metal can be considered as a set of ionic cores surrounded by a sea of electrons. However, as soon as you have ionic cores the electrons will be localised in their deep attractive potentials. Thus it is more correct to say that the ionic cores are "averaged out" to produce a *uniform background potential*, **Figure 4**. The electrons are assumed to move freely within this potential, and hence the cloud of electrons is called the *free electron gas*, this is the key entity for a physicist. Unlike the electrons in a real system the cloud of electrons is uniform, (ie has no underlying structure such as orbitals, only the electron density $\rho(r)$ matters, full stop).

In a real molecule (**Figure 5**) the total density varies, ie it is not uniform, for example patches become quite dense where there are bonds and nuclei, think of "lumpy custard", good custard of course has a uniform density (as does the free electron gas). When we write a wavefunction for *ab-initio* theories it depends on the (x, y, z) coordinates of *each* electron, we have a function of $3N$ variables (**Figure 6**), making the Schrödinger equation very hard to solve. However if we make the uniform background charge approximation we need only determine the variations in the density of the electron gas ie in terms of x, y, and z (**Figure 7**). The total density is a function of *just 3* coordinates! Think of solving the Schrödinger equation as like juggling balls, it is much easier to juggle three balls (DFT) than it is 300 balls (*Ab-initio* methods).

Thus the total energy of a molecule is dependent on the electron density (which is in turn position dependent). We say that the energy is a *functional* of the density (ie a function of a function), $E[\rho(r)]$. We represent a functional with square brackets. We also now know why it's called Density Functional Theory.

Just a note, remember $\rho(r)$ is the *total* density (it includes all the electrons), so the wavefunction which gives rise to this density is the total molecular wavefunction. Even though we write $E[\rho(r)]$ it's just the same old energy E that it was before, writing this way we are just emphasising its dependence on the density. However while

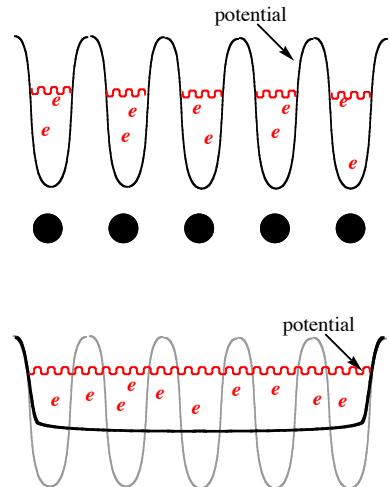


Figure 4 The sea of electrons in a uniform background potential (solid state)

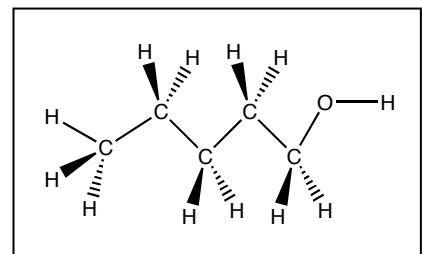


Figure 5 Molecule

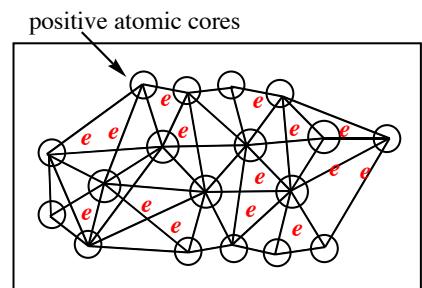


Figure 6 Explicit interactions

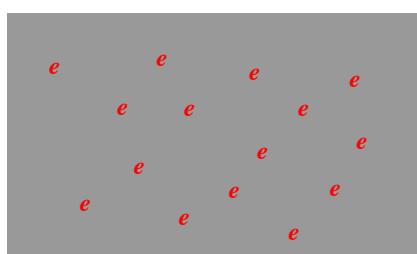


Figure 7 Electrons interacting with the uniform background charge

the total density is the density of interest, it is hard to use and so we expand it in terms of a set of basis functions and then work in that basis. A very good basis is the basis of atomic orbitals! In wavefunction theories the atomic orbital basis has a clear physical relevance, in DFT theory it is *only* a set of functions used to expand the density. There is still significant debate about the physical relevance of these functions. I'm not going to do this as it is complex, and not what this course is about. However, we can still *try* to write the basic Schrödinger equation in terms of the density.

Physics have proven conceptually that each unique density is derived from a unique potential and gives a unique energy (easy to assume, very very difficult to prove). However, no one knows the exact functional $E[\rho(r)]$ for molecules! (One of the most significant problems in theoretical chemistry today) We can make a very good guess at $E[\rho(r)]$ based on things we have already know.

We can write conceptually write the Schrödinger equation in terms of densities, ie as functionals;

$$E[\rho] = T[\rho] + E_{nn}[\rho] + E_{ne}[\rho] + J_{ee}[\rho] + K_{ee}[\rho]$$

where $T[\rho]$ is the kinetic energy functional of the electrons $E_{ne}[\rho]$ is the electron-nuclear potential energy functional, and the $E_{ee}[\rho]$ electron-electron potential energy functional is split into a coulomb component $J_{ee}[\rho]$ and exchange component, $K_{ee}[\rho]$. The nuclear-nuclear interaction energy is added later because it is just a fixed number because the nuclei are not moving. Some of these functionals are easy to write in terms of densities:

$$\begin{aligned} J_{ee}[\rho(r)] &= \sum_{i=1, j>i}^{N_e} \int \frac{\rho(r_i)\rho(r_j)}{|r_i - r_j|} dr_i dr_j \\ E_{ne}[\rho(r)] &= - \sum_{\alpha=1, i=1}^{N_n, N_e} \frac{1}{2M_\alpha} \int \frac{Z_\alpha \rho(r_i)}{|R_\alpha - r_i|} dr_i \end{aligned}$$

However, others are not so easy to write such as the exchange part of the electron-electron interactions, and the kinetic energy (because of the grad operator).

$$T[\rho(r)] = -\frac{1}{2} \sum_{i=1}^{N_e} \int \psi_i^* \nabla^2 \psi_i dr_i \text{ which cannot be written in terms of densities}$$

$$K_{ee}[\rho(r)] = ??? \text{ a functional which cannot be written in terms of densities}$$

We can however do a little better, we assume that one electron is whizzing around independently of all the other electrons who are whizzing around, ie the electrons are not "seeing" each other and $V_{ee}=0$. In this case (and only in this case) we can write an expression for $T_{ni}[\rho(r)]$ (ni = non interacting). Then we assume that if we turned V_{ee} on, that it would not effect $T[\rho(r)]$ by much, we would just add a small corrective term.

$$T[\rho] = T_{\text{non-interacting}}[\rho] + T_{\text{correction}}[\rho]$$

Collecting all the unknowns or difficult terms into one component we have:

$$E[\rho] = \underbrace{(T_{ni}[\rho] + E_{nn}[\rho] + E_{ne}[\rho] + J_{ee}[\rho])}_{\text{known}} + \underbrace{(K_{ee}[\rho] + T_c[\rho])}_{\text{unknown}}$$

$$E_{xc}[\rho] = K_{ee}[\rho] + T_c[\rho]$$

Where the unknown portion is normally termed the *exchange-correlation* functional. Note that this name is a misnomer, because $E_{xc}[\rho]$ contains the exchange (and correlation) component *and* a kinetic energy component. A better name would be "all the missing and difficult stuff." It has been a long hard road trying to work out a suitable form for this functional, and the problem has still not been solved! Solving this part of this equation would be Nobel prize material. This unknown bit is why DFT methods are less rigorous than *ab-initio* HF (even though HF is less accurate!)

This exchange-correlation functional $E_{xc}[\rho]$ is so important that all DFT methods are named for how they try to model it. Normally we assume the exchange-correlation functional $E_{xc}[\rho]$ can be split it into two components (which don't relate directly to the original components) called the exchange ($E_x[\rho]$) and correlation ($E_c[\rho]$) components,

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$$

Each of these is fit by a separate functional form, so when identifying an exchange-correlation functional, you identify the exchange part then the correlation part, **Table 1**. For example B3LYP means use B3 form for the exchange part and LYP form for the correlation part. Because the problem is still under development there are many versions of the exchange-correlation functional, and more are being developed while we speak. By this time next year there will very likely be several new functionals. Recently there has been a resurgence in the deveopment of functionals, and there are many new ones about!

You need to be aware that the form of many functionals is not based on the physics of the problem, we don't know what mathematical form $E_{xc}[\rho]$ should have. However, we do know what the boundary conditions should be and so these inform the choice of functionals.

The sophistication of functionals has been increased over time, those functionals that depend only on $\rho(r)$ are called *Local Density Approximation* or LDA functionals, those that depend on $\rho(r)$ and the gradient $\nabla\rho(r)$ are called *Generalised Gradient*

functional	exchange	correlation
<i>LDA functionals</i>		
SVWN	S	VWN
<i>GGA functionals</i>		
BLYP	B=B88	LYP
BP86		P86
BPW91		PW91
<i>Hybrid GGA functionals</i>		
B3LYP	B3	LYP
B3P86		P86
B3PW91		PW91
PBE0	PBE	PBE

Table 1 DFT functionals, the full names of the acronyms are given below.

exchange $E_x[\rho]$ functional

S	Slater
B=B88	Becke published 1988
PW91	Perdew & Wang published 1991
B3	Becke's 3-parameter hybrid (1993)
PBE	Perdew, Burke & Ernzerhof (1996)

correlation $E_c[\rho]$ functional

VWN	Vosko, Wilk & Nusair
LYP	Lee, Yang & Parr
P=P86	Perdew published 1986
PW91	Perdew & Wang published 1991
PBE	Perdew, Burke & Ernzerhof (1997)

Approximation or GGA functionals. Those that include a small portion of HF exchange (ie some of HF evaluation of K_{ee}) are called *Hybrid GGA* functionals.

B3LYP is a Hybrid-GGA functional and is the most commonly employed functional.

$$E_{XC}^{B3LYP}[\rho] = (1-a)E_X^{LSD} + aE_{XC}^{\lambda=0} + bE_{XC}^{B88} + cE_C^{LYP} + (1-c)E_C^{LSD} \quad a=0.20, b=0.72, c=0.81$$

We start with the exchange correlation from a uniform electron gas, E_{XC}^{LSD} . If we assume a non-interacting system ie correlation=0 then the only contribution to E_{xc} is the exchange, this can be computed exactly, it is the HF exchange for a single Slater determinant, $E_{XC}^{\lambda=0}$. E_X^{LSD} is the exact exchange from the uniform electron gas. So it is clear the first two terms balance exact and LDA exchange contributions. E_{XC}^{B88} is a correction by Becke. E_C^{LYP} is an expression for the correlation energy based on the correlation energy of a helium atom obtained using a correlated wave function theory. E_C^{LSD} is the exact correlation from the uniform electron gas. Thus these two terms balance a guess at "full" correlation with LSD correlation. This equation depends on three entirely empirical parameters, a, b and c. They were chosen based on selected atomization and ionization energies, and proton affinities. Notice that only a small amount of exact HF exchange has been included.

One of the problems of DFT is that new functionals come out all the time and you have little real idea of how good they are. However, there are some tried and tested functionals that you can be reasonably sure about how accurate they are. The exchange and correlation components of $E_{xc}[\rho]$ can to some extent be mixed but certain functionals are never matched together, for example S with a higher level correlation functional or VWN with a higher level exchange functional. Only calculations using exactly the same functionals should be compared.

Table 2 contains some data on the accuracy of various types of functional.[†] Generally Hybrid GGA functionals are the best. However, in most cases the performance of DFT functionals has been benchmarked against small organic molecules with atoms primarily from the first row, hence we simply don't know the accuracy of these methods when applied to transition metals, and heavier main group elements including those such as Si and P. Another problem is that the performance of DFT functionals has been benchmarked against geometries, and vibrational frequencies of minima, not transition states, or structures away from minima. Can we really trust these methods to give us good reaction barriers? Generally we assume they do, but if you want really accurate energies you must use more sophisticated methods that include more correlation.

functional	mean absolute deviation	maximum absolute deviation
<i>LDA functionally</i>		
SVWN or LDA	90.9	288.7
<i>GGA functionals</i>		
BLYP	7.1	28.4
BPW91	7.9	32.2
<i>Hybrid GGA functionals</i>		
B3LYP	3.1	20.1
B3PW91	3.5	21.8

Table 2 Comparison of performance of DFT Methods (kcal/mol)[†]

[†] Data taken from "Introduction to Computational Chemistry" by Frank Jensen, John Wiley & Sons, Chichester, 2003.

Meta GGA functionals include higher order derivatives of the electronic density. The second derivative of the electron density gives rise to the Laplacian ($\nabla^2 \rho$) which measures the local curvature of the density about a defined point, however, it is rather difficult to compute. Therefore, the related kinetic energy density (τ) is more frequently used, it carries essentially the same information and is easier to compute. (ψ_i are the occupied Kohn Sham orbitals)

$$\tau(r) = \sum_i^{\text{occ}} \frac{1}{2} |\nabla \psi_i(r)|^2$$

Inclusion of this additional derivative is, in theory, an improvement over GGA functionals as the kinetic energy density term provides more information than the gradient alone. Consequently this improvement should equate to a better description. Unfortunately early meta-GGA functionals exhibited only marginal improvements over GGA functionals with regards to certain characteristics (thermochemistry) whereas they performed poorly in other areas (geometries). Around the same time, hybrid GGA density functionals were breaking ground, providing high quality numerical results at a slightly higher computational cost in comparison to other GGA functionals. Such was the success of the hybrid density functionals, particularly the B3LYP functional, that the mGGA functionals became overshadowed.

The TPSS exchange-correlation functional, developed by Tao, Perdew, Staroverov and Scuseria, is a relatively recent mGGA that is implemented in the Gaussian computational chemistry suite. TPSS is a refinement of an earlier mGGA functional, PKZB (developed by Perdew, Kurth, Zupan and Blaha). They both have the same local exchange and correlation components however TPSS improves on a number of properties including the exchange energy component of PKZB which previously resulted in long bonds. TPSS has shown success in atomization energies, surface energies for solids and in obtaining accurate geometries for first row transition metal complexes (a particular trouble point for DFT). Further improvement of the TPSS functional comes with the addition of some small addition of HF exact exchange. The hybrid-meta-GGA functional, TPSSH has shown good performance in the computation of bioinorganic molecules.

Density functionals are good at accurately predicting short-range interactions however, this breaks down at longer range. Including 100 % HF exact exchange accurately predicts the asymptotic conditions, but this cannot simply be added into a density functional as error cancellations between the exchange and correlation functionals don't work properly. Exchange and correlation functionals must be matched up very carefully and HF exact exchange is generally added in small percentages. In an attempt to address this problem, groups have been actively looking at ways of introducing 100 % HF exact exchange (or a large fraction) at long-range. This series of approximations are known as long-range corrected hybrid density functionals.

The exchange-correlation operator is partitioned into a short-range (SR) and long-range (LR) term whereby the long-range electron-electron interactions are described by HF exact exchange whereas the short-range exchange and correlation terms are still approximated using traditional density functional approximations.

There are many variations of long-range corrected functionals however a set of functionals, implemented in Gaussian, showing promise are ω B97 and ω B97X developed by Chai and Head-Gordon. ω B97 and ω B97X are constructed around Becke's B97 GGA exchange-correlation functional. The range at which the SR-B97

exchange functional operates is dictated by the flexible enhancement factor (ω). ω B97X also has an additional adjustable fraction of short range HF exchange.

In spite of the name long range-corrected hybrid functionals still only describe medium-range interactions, tentatively assigned within the region of 3-5 Å. In fact all of the functionals described up to this point are either local or semi-local functionals. Long-range non-covalent interactions (~6 Å) such as dispersion are not accurately described (if at all). This failure stems from the fact that the even with the incorporation of non-local HF exact exchange in hybrid functionals, including LC-corrected, dispersion is related to electron-correlation and not exchange. These types of functionals are inherently unable to describe dispersion.

Dispersion interactions are the interaction between instantaneous dipole moments within the electron distributions of two atoms or molecules, the dispersion energy takes the form of a series expansion of which only the first term is normally used:

$$E_{\text{disp}} = \frac{-C_6}{R^6} + \frac{-C_8}{R^8} + \frac{-C_{10}}{R^{10}} + \dots$$

Dispersion is a consequence of many-particle (electron correlation). Commonly employed density functionals are successful in treating interactions that act over short length scales (<2 Å) but fail in the treatment of the dispersion attraction which is best observed over longer medium- (~2-5 Å) and long-range (> 5 Å) distances. This is because none of the typical components of a functionals is fully capable of acting over this range. Hybrid functionals include long-range behaviour through HF exchange but remain local in correlation and therefore are also unable to describe the R⁻⁶ asymptotic distance dependence of dispersion forces. Several conventional GGAs, meta-GGAs, hybrids and meta-hybrids have also been shown to reproduce weak van der Waals (dispersion) interactions in one or other molecular system in comparison MP2 and CCSD(T) reference data, however, the general consensus is that good performance of ‘standard’ functionals is fortuitous and most probably arises from error cancellation or in the case of the M0# series of Truhlar from the incorrect behaviour of the exchange functional.

Currently the accurate description of dispersion interactions is an active field with new and revised functionals being produced now! Here we will only introduce a subset of those available.

DFT-D is the most widely used implementation, it is adaptable for use with any density functional. A simple dispersion correction is added to the Kohn-Sham DFT total energy where E_{Disp} is an empirical dispersion correction given by (R_{ij} is the interatomic distance)

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{Disp}}$$

$$E_{\text{Disp}}^{D2} = -s_6 \sum_{i,j>i}^{N_{\text{at}}} \frac{C_6^{ij}}{R_{ij}^6} f_{\text{damp}}(R_{ij}) \quad \text{or} \quad E_{\text{Disp}}^{D3} = - \sum_{n=6,8} s_n \sum_{i,j>i}^{N_{\text{at}}} \frac{C_n^{ij}}{R_{ij}^n} f_{\text{damp}}(R_{ij}, s_{r,n})$$

In DFT-D2 C₆^{ij} denotes the dispersion coefficient for atom pair ij obtained from the geometric mean of tabulated elemental values familiar to those who carry out classical molecular dynamics. In order to avoid near-singularities for small R and electron correlation double-counting effects, a damping function f_{damp} is used. DFT-D3 is a refined method which incorporates a R-8 term in the dispersion series and adjusts the C₆^{ij} combination formula and dampening function. The individual atomic C₆^{ij} are interpolated from several reference values based upon coordination numbers

extracted from the molecular structure and thereby incorporate some awareness of the chemical environment. In both functions S_6 and S_n are global scaling factors that depend on the form of the functional used. Commonly employed density functionals that include a dispersion correction are; B97-D, wB97X-D, B3LYP-D, PBE-D, PBE0-D, BP86-D, B2PLYP-D and mPW2PLYP-D.

Another strategy to account for dispersion interactions has been developed by Zhao and Truhlar. Minnesota functionals form a series of functionals built around a meta-GGA functional, (denoted as M## where the ## relates to the year they were made available). For example, M06-L is a mGGA functional whereas M06-HF, which incorporates 100 % HF exchange is a hybrid meta GGA. There are two additional hybrid-meta-GGA functionals in this series; M06 and M06-2X which have smaller contributions of HF exact exchange (M06-2X having twice that of M06). In addition Zhao and Truhlar have also developed a long-range corrected Minnesota functional, M11. In all cases, the Minnesota class of functionals are heavily parameterized using experimental data.

Minnesota functionals are not corrected for dispersion in the same way as DFT-D, they still give relatively accurate results and have shown improvement over other popular functionals in describing non-covalent interactions between molecules. One flaw with such highly parameterised functionals is that there is no guarantee they will be suitable outside of their parameterisation set. That aside, M06-2X in particular, has shown promise in main-group thermochemistry and kinetics.

Very recently double hybrid functionals have been developed. As hybrid GGA functionals use the wavefunction method to give exchange exactly, double hybrids expand upon this and use MP2 theory to include correlation effects:

$$E_{xc} = (1 - c_x)E_x^{DFT} + c_x E_x^{HF} + (1 - c_c)E_c^{DFT} + c_c E_c^{MP2}$$

A large amount of exact exchange is included in these types of functionals to improve the self-interaction error typically associated with hybrid functionals. Inclusion of MP2 nonlocal correlation effects, essentially includes the unoccupied Kohn-Sham orbitals within the calculation. This allows for greater accuracy when computing kinetic barriers and diffuse orbitals. A further benefit from using double hybrid functionals is that dispersion forces can be computed more accurately than previous DFT methods although overall they are still underestimated.

Double hybrid functionals show superior performance to previous DFT methods however this comes at a large cost. Inclusion of MP2 correlation and increased quantities of exact exchange require considerable computational resources. Double hybrid calculations are plagued with difficulties in convergence and very large basis sets are required in order to obtain meaningful results.

Electron Correlation

Electron correlation refers to the fact that the presence of one electron will effect the position and behaviour of another electron, ie that their positions are correlated. Quantum mechanics states that two electrons cannot be at the same place at the same time, and ordinary columbic effects also tell us that two negative charges don't want to be close together. We also find that when a molecule is pulled apart the Slater determinant wavefunction is not sufficient and higher excited states need to be included. These are all forms of *correlation*.

Exchange Correlation and the Fermi Hole

This form of correlation relates to the spin of the electrons. If we start from the point that a wavefunction has a spatial and spin component:

$$\psi(x) = \chi(r)\sigma(s)$$

And if we have two electrons we need to write the wavefunction as a Slater determinant of these orbitals:

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_i(x_1)\psi_j(x_2) - \psi_j(x_1)\psi_i(x_2)]$$

Forming the probability density, which is the probability of finding electron i in dx_1 of orbital ψ_i and electron j in dx_2 of orbital ψ_j at the same time:

$$\begin{aligned} \rho(x_1, x_2) &= \int \Psi^2(x_1, x_2) dx_1 dx_2 \\ &= \frac{1}{2} \int [\psi_i(x_1)\psi_j(x_2) - \psi_j(x_1)\psi_i(x_2)][\psi_i(x_1)\psi_j(x_2) - \psi_j(x_1)\psi_i(x_2)] dx_1 dx_2 \\ &= \frac{1}{2} \left[\int \psi_i(x_1)\psi_j(x_2)\psi_i(x_1)\psi_j(x_2) dx_1 dx_2 + \int \psi_j(x_1)\psi_i(x_2)\psi_j(x_1)\psi_i(x_2) dx_1 dx_2 \right] \\ &\quad - \left[\int \psi_j(x_1)\psi_i(x_2)\psi_i(x_1)\psi_j(x_2) dx_1 dx_2 - \int \psi_i(x_1)\psi_j(x_2)\psi_j(x_1)\psi_i(x_2) dx_1 dx_2 \right] \\ &= \frac{1}{2} \left[\int |\psi_i(x_1)|^2 |\psi_j(x_2)|^2 dx_1 dx_2 + \int |\psi_j(x_1)|^2 |\psi_i(x_2)|^2 dx_1 dx_2 \right] \\ &\quad - \left[\int \psi_j(x_1)\psi_i(x_2)\psi_i(x_1)\psi_j(x_2) dx_1 dx_2 - \int \psi_i(x_1)\psi_j(x_2)\psi_j(x_1)\psi_i(x_2) dx_1 dx_2 \right] \\ \rho(x_1, x_2) &= \frac{1}{2} \left[\int |\psi_i(x_1)|^2 |\psi_j(x_2)|^2 dx_1 dx_2 + \int |\psi_j(x_1)|^2 |\psi_i(x_2)|^2 dx_1 dx_2 \right] \\ &\quad - 2 \int \psi_j(x_1)\psi_i(x_2)\psi_i(x_1)\psi_j(x_2) dx_1 dx_2 \end{aligned}$$

Taking the final expression and expanding for the spatial and spin orbitals, and knowing that spin functions are orthonormal for the first term:

$$\begin{aligned} \int |\psi_i(x_1)|^2 |\psi_j(x_2)|^2 dx_1 dx_2 &= \int |\chi_i(r_1)\sigma_i(s_1)|^2 |\chi_j(r_2)\sigma_j(s_2)|^2 dr_1 ds_1 dr_2 ds_2 \\ &= \int |\chi_i(r_1)|^2 \bullet \int |\chi_j(r_2)|^2 dr_2 \bullet \int |\sigma_i(s_1)|^2 ds_1 \int |\sigma_j(s_2)|^2 ds_2 \\ &= \rho_i(r_1) \bullet \rho_j(r_2) \bullet 1 \bullet 1 \end{aligned}$$

for the second term:

$$\int |\psi_j(x_1)|^2 |\psi_i(x_2)|^2 dx_1 dx_2 = \rho_j(r_1) \bullet \rho_i(r_2) \bullet 1 \bullet 1$$

for the third term:

$$\begin{aligned}
& \int \psi_j(x_1) \psi_i(x_1) \psi_i(x_2) \psi_j(x_2) dx_1 dx_2 \\
&= \int \chi_j(r_1) \sigma_j(s_1) \chi_i(r_1) \sigma_i(s_1) \chi_i(r_2) \sigma_i(s_2) \chi_j(r_2) \sigma_j(s_2) dr_1 ds_1 dr_2 ds_2 \\
&= \int \chi_j(r_1) \chi_i(r_1) dr_1 \bullet \int \chi_i(r_2) \chi_j(r_2) dr_2 \bullet \int \sigma_j(s_1) \sigma_i(s_1) ds_1 \bullet \int \sigma_i(s_2) \sigma_j(s_2) ds_2 \\
&\text{if } \sigma_j = \sigma_i \quad \int \sigma_i \sigma_i = 1 \\
&\quad = \int \chi_j(r_1) \chi_i(r_1) dr_1 \bullet \int \chi_i(r_2) \chi_j(r_2) dr_2 \bullet \int \sigma_i(s_1) \sigma_i(s_1) ds_1 \bullet \int \sigma_i(s_2) \sigma_i(s_2) ds_2 \\
&\quad = \int \chi_j(r_1) \chi_i(r_1) dr_1 \bullet \int \chi_i(r_2) \chi_j(r_2) dr_2 \bullet 1 \bullet 1 \\
&\text{if } \sigma_j \neq \sigma_i \quad \int \sigma_j \sigma_i = 0 \\
&\quad = 0
\end{aligned}$$

Summarising this information, if the spins are different then the first two terms remain and the third term is zero. If the spins are the same the last term is present:

$$\begin{aligned}
\rho(x_1, x_2) &= \frac{1}{2} \left[\int |\psi_i(x_1)|^2 |\psi_j(x_2)|^2 dx_1 dx_2 + \int |\psi_j(x_1)|^2 |\psi_i(x_2)|^2 dx_1 dx_2 \right] \\
&\text{if } \sigma_j \neq \sigma_i \quad \rho(x_1, x_2) = \frac{1}{2} \left[\rho_i(r_1) \bullet \rho_j(r_2) + \rho_j(r_1) \bullet \rho_i(r_2) \right] \\
&\quad \left[\int \chi_i(r_1) \chi_i(r_1) dr_1 \bullet \int \chi_j(r_2) \chi_j(r_2) dr_2 \right] \\
&\text{if } \sigma_j = \sigma_i \quad \rho(x_1, x_2) = \frac{1}{2} \left[+ \int \chi_j(r_1) \chi_j(r_1) dr_1 \bullet \int \chi_i(r_2) \chi_i(r_2) dr_2 \right. \\
&\quad \left. - 2 \int \chi_j(r_1) \chi_i(r_1) \chi_i(r_2) \chi_j(r_2) dr_1 dr_2 \right]
\end{aligned}$$

Now the probability of having two electrons in the same orbital with the same spin is zero:

$$\begin{aligned}
&\text{if } \sigma_j = \sigma_i \\
&\quad \left[\int \cancel{\chi_i(r_1)} \cancel{\chi_i(r_1)} dr_1 \bullet \int \cancel{\chi_i(r_2)} \cancel{\chi_i(r_2)} dr_2 \right] \\
\rho(x_1, x_1) &= \frac{1}{2} \left[+ \int \cancel{\chi_i(r_1)} \cancel{\chi_i(r_1)} dr_1 \bullet \int \cancel{\chi_i(r_2)} \cancel{\chi_i(r_2)} dr_2 \right. \\
&\quad \left. - 2 \int \cancel{\chi_i(r_1)} \cancel{\chi_i(r_1)} dr_1 \bullet \int \cancel{\chi_i(r_2)} \cancel{\chi_i(r_2)} dr_2 \right] = 0
\end{aligned}$$

What this means is that if the two electrons have the same spin then the chance of finding them together is zero, that is they are correlated. Electrons of the same spin "correlate" so as not to occupy the same space at the same time, this depleted probability is called the *Fermi hole*. This type of correlation is called *exchange or Fermi correlation*. This is a direct consequence of the Pauli exclusion principle, two electrons cannot have identical quantum numbers. **In HF theory same spin electrons in the same orbital have exchange or Fermi correlation, or exhibit a Fermi hole.**

if $\sigma_j \neq \sigma_i$

$$\begin{aligned} \rho(x_1, x_2) &= \frac{1}{2} [\rho_i(r_1) \bullet \rho_i(r_2) + \rho_i(r_1) \bullet \rho_i(r_2)] \\ &= \rho_i(r_1) \bullet \rho_i(r_2) \\ &\neq 0 \end{aligned}$$

If the two electrons (in the same orbital) have different spin then they are not correlated, there is a non-zero probability that the two electrons can be found "on-top" of each other. In addition the probability is a simple product of the individual electron probabilities. This means that if each electron was by itself then it would still have the same chance of being in that place, the presence of the second electron is irrelevant to determining the first electron's probability, these electrons are uncorrelated. Thus electrons of different spin can occupy the same spacial orbital or same part of space. **In HF theory different spin electrons in the same orbital are not correlated.**

The Self Interaction

Now consider what effect the wavefunction has on the Coulomb interaction. The important part of the HF equations are the two electron operators.

$$\begin{aligned} (J_{ee} - K_{ee}) &= \frac{1}{2} \sum_{i,j}^{N_e} \int \psi_i^*(x_1) \psi_i(x_1) \frac{1}{|r_1 - r_2|} \psi_j^*(x_2) \psi_j(x_2) dx_1 dx_2 \\ &\quad - \frac{1}{2} \sum_{i,j}^{N_e} \int \psi_j^*(x_1) \psi_i(x_1) \frac{1}{|r_1 - r_2|} \psi_i^*(x_2) \psi_j(x_2) dx_1 dx_2 \\ &= \frac{1}{2} \sum_{i,j}^{N_e} \int \chi_i^*(x_1) \chi_i(x_1) \frac{1}{|r_1 - r_2|} \chi_j^*(x_2) \chi_j(x_2) dx_1 dx_2 \bullet \int \sigma_i(s_1) \sigma_i(s_1) ds_1 \bullet \int \sigma_j(s_2) \sigma_j(s_2) ds_2 \\ &\quad - \frac{1}{2} \sum_{i,j}^{N_e} \int \chi_j^*(x_1) \chi_i(x_1) \frac{1}{|r_1 - r_2|} \chi_i^*(x_2) \chi_j(x_2) dr_1 dr_2 \bullet \int \sigma_j(s_1) \sigma_i(s_1) ds_1 \bullet \int \sigma_j(s_2) \sigma_i(s_2) ds_2 \\ &= \frac{1}{2} \sum_{i,j}^{N_e} \int \chi_i^*(x_1) \chi_i(x_1) \frac{1}{|r_1 - r_2|} \chi_j^*(x_2) \chi_j(x_2) dx_1 dx_2 \bullet 1 \bullet 1 \\ &\quad - \frac{1}{2} \sum_{i,j}^{N_e} \int \chi_j^*(x_1) \chi_i(x_1) \frac{1}{|r_1 - r_2|} \chi_i^*(x_2) \chi_j(x_2) dr_1 dr_2 \bullet \int \sigma_j(s_1) \sigma_i(s_1) ds_1 \bullet \int \sigma_j(s_2) \sigma_i(s_2) ds_2 \end{aligned}$$

If the spin of the two electrons is the same then we recover the full spatial part of the equation (ie both J and K) as shown below, however if the spins are different we loose the second spatial (K or exchange) term:

if $\sigma_j = \sigma_i$ $\int \sigma_j \sigma_i = 1$

$$\begin{aligned} (J_{ee} - K_{ee}) &= \frac{1}{2} \sum_{i,j}^{N_e} \int \chi_i^*(x_1) \chi_i(x_1) \frac{1}{|r_1 - r_2|} \chi_j^*(x_2) \chi_j(x_2) dx_1 dx_2 \\ &\quad - \frac{1}{2} \sum_{i,j}^{N_e} \int \chi_j^*(x_1) \chi_i(x_1) \frac{1}{|r_1 - r_2|} \chi_i^*(x_2) \chi_j(x_2) dr_1 dr_2 \end{aligned}$$

if $\sigma_j \neq \sigma_i$ $\int \sigma_j \sigma_i = 0$

$$(J_{ee} - K_{ee}) = \frac{1}{2} \sum_{i,j}^{N_e} \int \chi_i^*(x_1) \chi_i(x_1) \frac{1}{|r_1 - r_2|} \chi_j^*(x_2) \chi_j(x_2) dx_1 dx_2$$

This is amazing! **Exchange terms exist only for electrons of the same spin.** So in the manifold of all the electrons with α spin, the electrons can exchange, and in the manifold of all the electrons with β spin the electrons can exchange. But the exchange of α and β spin electrons contributes nothing.

Notice that our summation does not exclude $i=j$. As ρ_i represents electron i in orbital ψ_i and As ρ_j represents electron j in orbital ψ_j , if we have $i=j$ then this **represents an electron interacting with itself**. An electron interacting with itself must have the same spin ($\sigma_i = \sigma_i$), back to the HF Coulomb and Exchange terms we obtain:

$$\begin{aligned} (J_{ee} - K_{ee}) &= \frac{1}{2} \sum_i^{N_e} \int \chi_i^*(r_1) \chi_i(r_1) \frac{1}{|r_1 - r_2|} \chi_i^*(r_2) \chi_i(r_2) dr_1 dr_2 \\ &\quad - \frac{1}{2} \sum_i^{N_e} \int \chi_i^*(r_1) \chi_i(r_1) \frac{1}{|r_1 - r_2|} \chi_i^*(r_2) \chi_i(r_2) dr_1 dr_2 \\ &= 0 \end{aligned}$$

Thus at the HF level J_{ee} and K_{ee} cancel each other out. This is great for HF theory but we still have the **non-physical Coulomb self interaction and self-Exchange** terms. These terms become a large problem for DFT theory and are known as the *self-interaction problem*.

Another common way of explaining this problem is the following. In DFT we are dealing with densities and not orbitals, and the self consistent field approach gives us the electron density of one electron interacting with the average of all the electrons over all space. This average includes all electrons (the total density divided by the number of electron) so it already includes the electron we are considering! The distribution of electron one includes a component that is interacting with itself. This interaction is un-physical, strictly speaking we should describe the distribution of the electron with respect to all *other* electrons.

Coulomb Correlation

If we have two electrons in two different orbitals, and they are of different spin then evaluating the two electron terms we get the Coulomb operator by itself:

$$\begin{aligned} \text{if } \sigma_j \neq \sigma_i \quad \int \sigma_j \sigma_i = 0 \\ (J_{ee} - K_{ee}) &= \frac{1}{2} \sum_{i,j}^{N_e} \int \chi_i^*(x_1) \chi_i(x_1) \frac{1}{|r_1 - r_2|} \chi_j^*(x_2) \chi_j(x_2) dx_1 dx_2 \\ &= \frac{1}{2} \sum_{i,j}^{N_e} \int \frac{\rho_i(x_1) \rho_j(x_2)}{|r_1 - r_2|} dx_1 dx_2 \end{aligned}$$

If we have two electrons in two different orbitals, and they are of the same spin then we get the Coulomb and Exchange operations:

$$\begin{aligned} \text{if } \sigma_j = \sigma_i \quad \int \sigma_j \sigma_i = 1 \\ (J_{ee} - K_{ee}) &= \frac{1}{2} \sum_{i,j}^{N_e} \int \chi_i^*(x_1) \chi_i(x_1) \frac{1}{|r_1 - r_2|} \chi_j^*(x_2) \chi_j(x_2) dx_1 dx_2 \\ &\quad - \frac{1}{2} \sum_{i,j}^{N_e} \int \chi_j^*(x_1) \chi_i(x_1) \frac{1}{|r_1 - r_2|} \chi_i^*(x_2) \chi_j(x_2) dr_1 dr_2 \end{aligned}$$

This case relates back to the density discussion: in HF theory different spin electrons are not correlated, the Coulomb expression above can be resolved in terms of non-correlated densities (they still interact via the Coulomb term) thus there is still electron-electron Coulomb repulsion. But there is no *Coulomb correlation*. ie we can still write the equation as densities and we do not need to resort to an orbital description. **HF completely neglects the Coulomb correlation.**

In terms of magnitude the Fermi hole dominates by far the Coulomb hole. **The Fermi hole integrates to (minus) one electron.** So we can think of electrons interacting with the Fermi hole (a bit like an electron interacting with a +1 ion!) **The Coulomb hole integrates to zero.** This doesn't mean it is zero, but rather that the positive patches are cancelled out by negative patches overall. In DFT the Fermi and Coulomb holes combine to form the "total" exchange correlation hole.

Dynamic and Static Correlation

Another way of dividing correlation is into two types, short range and long range, although the distinction is not clear in the "middle ground". The correlation energy of a system is *defined* as the correct total energy minus the HF energy. Thus the "correlation" energy encompasses *everything* that makes the HF energy incorrect.
 $E_{\text{correlation}} = E_{\text{total}} - E_{\text{HF}}$

Short range or *dynamic correlation* occurs when the two electrons are confined to the same local area, for example two electrons in an orbital (or even in a bond) will correlate their motion, so as to not be in the same place at the same time. In fact they will prefer to be as far apart as possible due to their coulomb repulsion, it is the attraction for the nuclei that keep them in the bond or orbital. Thus *dynamic correlation* is about electrons "moving" so as to avoid each other. This type of correlation is recovered a little by DFT and MP2 level methods.

Long range or *static correlation* is about a failure of lower level methods because of approximations that have been introduced. For example HF does not explicitly treat the interaction of each electron with each other electron, it takes all the "other" electrons, averages over them, and then works out the interaction of each specific electron with the average of all the other electrons. It also does not correctly describe the distribution of electrons as a molecule dissociates. It is not part of this course to discuss the different ways of improving on the correlation. They are very complicated!! However you do need to be aware of the rough sequence of methods that provides ever improving contributions to the correlation energy. There is a sequence of methods called, the MP series which use a perturbative approach, you will mostly meet MP2 but there are the MP3 and MP4 methods (we don't go higher than MP4 for reasons I'm not going to go into).

Next come the *configuration interaction* methods, these include the effects of allowing electrons within the molecule to be excited into upper energy levels, a *single*

Methods (% correlation included):
HF
DFT[LDA/SVWN]
DFT[GGA]
DFT[hybrid GGA]
MP2 (94.0%)
MP3/MP4 (99.5/99.7%)
CISD (94.5%)
MCSCF
MCPF
CISDT (95.8%)
CCSD (98.3%)
CCSD(T) (99.7%)
QCISDT (99.9%)

Table 3 Computational methods in increasing complexity and accuracy

excitation allows one electron (from any occupied orbital) to be excited (into any unoccupied orbital), a *double excitation* allows two electrons to be excited at the same time, and so on. CISD is a Configuration Interaction method that includes Single and Double excitations. CCSD is a Coupled Cluster method (just another way of including multiple configurations) that includes Single and Double excitations. A T in brackets, (T), means triple excitations have been included in an approximate way, eg CCSD(T) method. Normally we don't include more than triple excitations, but it is possible to include triple and quadruple excitations explicitly, eg QCISDT. Thus you can see how a sequence of methods builds up around a particular way of treating the extra configurations, eg CCSD -> CCSD(T) -> CCSDT and CIS -> CISD -> CISDT -> CISDTQ. The method called "Full CI" includes all possible excitations, and thus it recovers all of the correlation in a system. Unfortunately this method is so expensive it can only be carried out for the smallest systems. Full CI recovers the correct total energy. **Table 3** lists methods in terms of their increasing sophistication and accuracy

Geometries at the HF, DFT and MP2 Level

Now we will consider how accurate the HF, DFT and MP2 methods are for predicting structures in general. When choosing a method, one that reaches an accuracy of ± 0.01 Å and 2 degrees in structures is considered reasonable. The first few lower level computational methods that I mentioned earlier are HF, DFT[LDA], DFT[GGA], DFT[Hybrid GGA] and MP2. These are ordered in a rough sense of increasing accuracy ie increasing recovery of correlation. Improving the basis set will in most cases improve geometries and frequencies. This ordering however is *general*, there are quite common exceptions. In addition, every method has some pathological cases where they fail, and fail badly. In **Table 4** a summary of the relative accuracy of the various methods is presented.

As a rough guide the application of these methods can be divided into the treatment of main group elements (organic compounds), transition metals (with d electrons), and the treatment of later metals such as the Lanthanides and actinides (with f electrons). When looking at organometallic complexes the errors will in general be larger because there are two sources, that due to the transition metal and that due to the organic ligand.

Method	main group E	3d TM	later TM	Lanthanides & Actinides
HF	single bonds too short (-0.02Å) multiple bonds poor (not enough correlation)	M-L too long (0.1 to 0.3Å)	same as 3d	M-L too short* (-0.02Å)
DFT(LDA)	E-H too long E-E too short E=E good E≡E too long errors range $\approx \pm 0.02$ Å	better than HF weak bonds too short (M-CO, M-NO) strong bonds good (M-Cl, M-OH) M=E too long	same as 3d	M-L too long* (+0.02Å)
DFT(GGA)	overall better than LDA but can overcompensate leading to larger errors E-H good E-E too long E=E good E≡E too long	bonds longer than LDA good weak bonds poor strong bonds errors in E contribute to M-E errors overall errors $\approx \pm 0.03$ -0.05Å	same as 3d	M-L too long* (+0.04Å)

	overall errors $\approx \pm 0.02$ BLYP less reliable than BP86 or BPW91	BP86 preferred		
DFT (Hybrid GGA)	50% better than GGA's error same as for crystal structures \approx CCDS(T) cc-pVQZ convergence faster	good B3LYP & B3PW91 preferred	M-E poor except: M-C good better than MP2	M-L too long* ($+0.02\text{\AA}$)
MP2	bonds slightly too long ($+0.01\text{\AA}$)	M-L too short poor errors can exceed $\pm 0.1\text{\AA}$	good	

Table 4 Accuracy of HF, DFT and MP2 for various systems.

*results from a single comparison based on UF₆, NpF₆ and PuF₆.

You should know the general accuracy of a particular method, the best method for each type of problem in addition to knowing the particular areas in which each method fails and why they fail.

For example MP2 methods fail for 3d TMs, errors can exceed 0.1 Å and the reason for this is the presence of low lying electronic states which are almost degenerate with the true ground state. The Hybrid methods perform extremely well for both main group atoms and transition metals and are as good as, and sometimes better than the MP2 method, and at a much lower level of cost! Hence most studies of inorganic systems containing a metal use a Hybrid GGA. The most often used Hybrid GGAs are B3LYP and BPE, so you need to know these acronyms. Below the table are listed key areas where computing structures may be problematic.

Key Problematic Cases:

Dispersion & van der Waals interactions: are not recovered by DFT and HF methods (dispersion effects are induced dipole interactions). MP2 is the lowest level method able to treat such systems.

Multiple bonds: multiple bonds have low lying π^* orbitals which means that there will significant contributions from low lying excited states to the ground state description. This includes ligands that undergo backbonding with metals, and aromatic systems. Methods that do not include correlation cannot treat multiple bonds well. The DFT(Hybrid GGA) and MP2 methods are best for treating first and second row organic systems. (For TM see below)

First row TM: Transition metals are difficult to treat because of the low lying degeneracies that can occur due to partial occupation of the dAO manifold, methods that include some "static" correlation must be used before transition metals will be accurately described. The 3d transition metals are particularly difficult to treat because there are no inner electrons of the same angular momentum, meaning that they interact with the core far more than the 4d and 5d transition metals. HF or low level DFT is not good. MP2 methods can fail badly (include mainly dynamic correlation), the *MP2 method cannot treat a multiple bond to a 3d TM*, it does not recover enough of the correlation due to the low lying unoccupied π^* orbitals. DFT(Hybrid GGA) is much better.

H-bonding: is not well described using HF or DFT(LDA) or DFT(GGA), it is reasonably well described by the Hybrid GGA functionals and the MP2 method. The electron cloud of the H atom and the lone pair donor interact introducing significant

"dynamic" correlation effects, and hence inclusion of "exchange" in Hybrid GGA improves DFT description.

Excited States: Not treated by HF or MP2 which are single reference methods, DFT can be used to look at excited states using time dependent TDDFT, but this field is in its infancy. First real methods for treating excited states are CI (configuration interaction) and AS (active space) methods.

Open shell systems: are *always* problematic. These are worst for HF and MP2 (see configuration interaction)

Relativistic Effects: are important for 4d and 5d TM, Lanthanides and actinides, and for heavy main group elements, and must be included. For example, there is a relativistic contraction of 0.06Å in the W-C bond of W(CO)₆. Luckily this can be achieved relatively easily by using relativistic pseudo-potentials in most cases. Where spin orbit coupling is strong a new term has to be introduced into the Hamiltonian, or the Dirac-Fock equation used.

A specific example: Cr(CO)₆

	Cr-C		C-O	
HF	2.010/2.017/1.970	long	1.111/1.111/1.118	short
DFT(SVWN)	1.865/1.866	short	1.145	close
DFT(BLYP)	1.942/1.937	long	1.157/1.164	long
DFT(B3LYP)	1.927/1.929/1.921	long	1.142/1.150/1.155	long
MP2	1.862/1.874	short	1.154	long
CCSD(T)	1.939	close	1.178	long!
exp	1.918	-	1.141	-

Table 5 Comparison of theoretical methods for Cr(CO)₆[‡]

[‡] Data taken from "A Chemists Guide to Density Functional Theory" Second Edition, by W. Koch and M. Holthausen, John Wiley & Sons, Weinheim, 2002.

Appendix 1: Understanding the Electron

As an analogy lets consider an excited child (it's their birthday) and they are having a special lunch at Pizza Hut, and because it is their birthday they are allowed as much snow-freeze as they like. Over half an hour we might expect to find the child close to the snow-freeze machine, but they will also track backwards and forwards to their table, and they might go further a field exploring the restaurant. If we were to mark the position of the child on the floor of the restaurant at given time intervals (say every minute) we would get a scatter of points, as in **Figure 8(a)**. If we were to divide the floor of the restaurant into concentric circles, 1m, 2m, 3m etc out from the snow-freeze machine and then total all the times the child was in a particular ring we would get a graph like that of **Figure 8(b)**. However we also need to normalise the graph for the increasing area covered by each ring and we get **Figure 8(c)**.

This graph gives a probability for the child to be in a particular ring, per unit area of that ring. By analogy we can think of the electron as having a probability of being in a certain volume shell about a nucleus. When we normalise for the increasing volume of each shell we have what is called a probability density distribution (*density* just referring to the fact we have a number divided by a volume, *probability* referring to the fact we have a "histogram", and *distribution* referring to the fact that the variable is continuous and normalised). The electron is most likely to be found near the nucleus, and is less likely to be found further away.

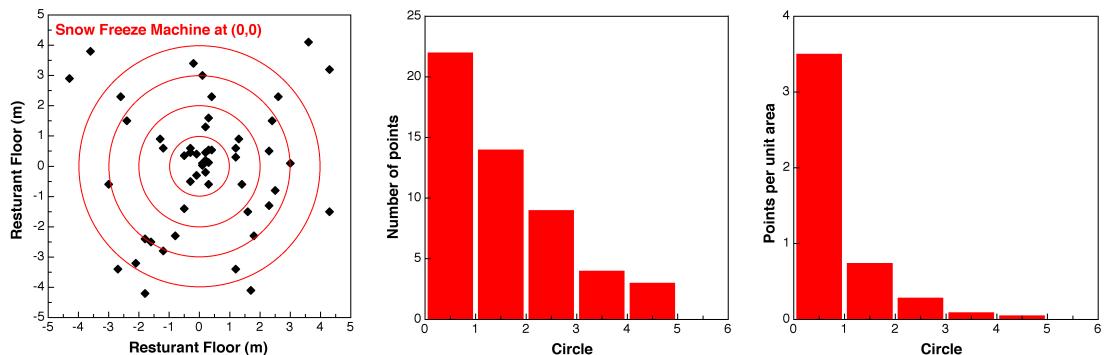


Figure 8 Probability density distributions (a) Distribution (b) Histogram (c) Normalised distribution

Appendix 2: The One Electron Orbitals

It is now worth coming back to talk about the wavefunction. The total wavefunction describes the whole molecule. We often make an approximation and say that this wavefunction can be modelled or described using a representation based on the atomic orbitals of all the atoms that make up that molecule. You might think that a simple product of all the atomic orbitals would be a good representation (where $\psi_i(e_i)$ is an orbital):

$$\Psi_{molecule} = \psi_1(e_1)\psi_2(e_2)\psi_3(e_3)\cdots\psi_n(e_n) = \prod_{i=1}^{N_p} \psi_i(e_i)$$

However, you would be wrong. The wavefunction has to satisfy the antisymmetry principle, that swapping any two electron labels leaves the wavefunction unchanged except for a negative sign. However a wavefunction which does this can be constructed, one such wavefunction for 2 electrons in 2 orbitals is shown below:

$$\Psi(e_1, e_2) = \frac{1}{\sqrt{2}} [\psi_1(e_1)\psi_2(e_2) - \psi_1(e_2)\psi_2(e_1)]$$

we require: $\Psi(e_1, e_2) = -\Psi(e_2, e_1)$

all I have done here is swap the electron labels ie swapped e_2 for e_1 :

$$-\Psi(e_2, e_1) = \frac{-1}{\sqrt{2}} [\psi_1(e_2)\psi_2(e_1) - \psi_1(e_1)\psi_2(e_2)]$$

and now I have taken the minus sign inside the bracket:

$$-\Psi(e_2, e_1) = \frac{1}{\sqrt{2}} [-\psi_1(e_2)\psi_2(e_1) + \psi_1(e_1)\psi_2(e_2)] = \Psi(e_1, e_2)$$

If all that is a bit confusing don't worry, it is background material and will not be examined. Notice that *the wavefunction is composed of sums of products of orbitals.*

$$\Psi(e_1, e_2) = \frac{1}{\sqrt{2}} \left[\underbrace{\psi_1(e_1)\psi_2(e_2)}_{product} - \underbrace{\psi_1(e_2)\psi_2(e_1)}_{product} \right]_{sum}$$

here is the start of the equation for three electrons in three orbitals:

$$\Psi(e_1, e_2, e_3) = \frac{1}{\sqrt{6}} \left[\underbrace{\psi_1(e_1)\psi_2(e_2)\psi_3(e_3)}_{product} - \underbrace{\psi_1(e_1)\psi_2(e_3)\psi_3(e_2)}_{product} + \underbrace{\psi_1(e_3)\psi_2(e_1)\psi_3(e_2)}_{product} + \dots \right]_{sum}$$

notice that I only ever swap two labels, eg we start with the first term: $\psi_1(e_1)\psi_2(e_2)\psi_3(e_3)$ then I swap e_2 for e_3 to get the second term: $\psi_1(e_1)\psi_2(e_3)\psi_3(e_2)$ (which has a minus sign because I swapped 2 electrons). To get the third term: $\psi_1(e_3)\psi_2(e_1)\psi_3(e_2)$ I have swapped e_1 for e_3 from the second term, this is two swaps away from the first term so that is (-1) for first swap and (-1) for the second swap, which gives me +1 so this term is positive. It goes on like this until all the possible combinations have been worked out.