

An Introduction to Density Functional Theory (DFT)

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This handout covers two lectures of the TMCS course ELECTRONIC STRUCTURE THEORY. Additional recommended reading is Koch and Holthausen's book on the subject¹ and for a reference on TD-DFT see Gross².

¹ W. Koch and M. C. Holthausen. *A Chemist's Guide to Density Functional Theory, 2nd edition*. Wiley, 2002

² M.A.L. Marques, C.A. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E.K.U. Gross. *Time-Dependent Density Functional Theory*. Springer-Verlag, 2006

Lecture 1. Hartree-Fock: a Reminder

A brief recap of the time-independent, non-relativistic, Born-Oppenheimer Hamiltonian:

$$\hat{H} = \hat{H}_{1e} + V_{ee}$$

Here one operator \hat{H}_{1e} does not contain electron-electron terms

$$\hat{H}_{1e} = \sum_i h(i) = \sum_i (\nabla_i^2 - \sum_n \frac{Z_n}{r_{in}})$$

Summation is over electrons (i) and nuclei (n). The second operator describes the Coulomb energy and the exchange energy terms, respectively:

$$\langle \Phi_{SD} | V_{ee} | \Phi_{SD} \rangle = \sum_{i < j} \langle \varphi_i \varphi_j | r_{12}^{-1} | \varphi_i \varphi_j \rangle - \sum_{i < j} \langle \varphi_j \varphi_i | r_{12}^{-1} | \varphi_i \varphi_j \rangle$$

In a Hartree-Fock (HF) calculation the objective is to minimize the energy with respect to the orbitals. The Slater determinant Φ_{SD} is the exact wavefunction of n non-interacting electrons moving in the mean-field of the effective potential.

In HF theory the wavefunction is used as the central quantity. The reason is that once we know (or have a good approximation to it) we have access to all information that can be known about this particular state. However, the wavefunction cannot be probed directly through experiment and depends on $4N$ variables, (three spatial and one spin variable for each of the N electrons).

Electron Density as a Basic Variable

Rather than the wavefunction, we would like to use the electron density, $\rho(\vec{r})$, since it depends only on three spatial variables. We will show that the electron density contains all the necessary ingredients for setting up a specific Hamiltonian to describe the system.

1. Integration of the density gives the number of electrons

$$\int \rho(r) dr = N$$

2. $\rho(r)$ has maxima, that are actually cusps, only at the positions of the nuclei

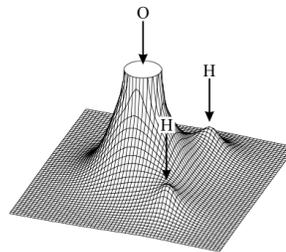


Figure 1: Electron density of a water molecule showing values of $\rho(r)$ projected onto the plane, which contains the nuclei (large values near the oxygen atom are cut out). From ref. 1

3. The density at the position of the nucleus contains information about the nuclear charge, Z_n

$$\lim_{r_{in} \rightarrow 0} \left[\frac{\partial}{\partial r} + 2Z_n \right] \rho(r) = 0$$

The Hohenberg-Kohn Theorems

DFT was given a formal footing by the two existence theorems introduced by Hohenberg and Kohn in 1964.³ Walter Kohn shared the Nobel Prize in Chemistry with John Pople in 1998.

The First Hohenberg-Kohn Theorem (HK1) states that the density $\rho(r)$ uniquely determines the Hamiltonian

That the electron density uniquely determines the Hamilton operator (and all properties of the system) can be proven by *reductio-ad-absurdum*: Suppose we have two different n -electron Hamiltonians $\hat{H}_1 \neq \hat{H}_2$ with exact ground-state solutions $\hat{H}_1 \Psi_1 = E_1 \Psi_1$ and $\hat{H}_2 \Psi_2 = E_2 \Psi_2$

If both wavefunctions possess the same electron densities $\Psi_1 \rightarrow \rho$ and $\Psi_2 \rightarrow \rho$, then \hat{H}_1 and \hat{H}_2 can only differ in their nuclear potentials. With $\hat{H}_1 \neq \hat{H}_2$ and recalling the variational theorem:

$$\langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle > E_1$$

Since we can write that $\hat{H}_1 = \hat{H}_2 + [\hat{H}_1 - \hat{H}_2]$ substituting into the expression above:

$$\langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \rangle > E_1$$

Since $\langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle = E_2$ this becomes

$$E_2 + \langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \rangle > E_1$$

Remember that only nuclear terms will differ, we can express the term in brackets as:

$$E_2 + \int d\vec{r} \rho(\vec{r}) v_1(\vec{r}) - \int d\vec{r} \rho(\vec{r}) v_2(\vec{r}) > E_1$$

Combining the nuclear potential terms:

$$\int d\vec{r} \rho(\vec{r}) v_1(\vec{r}) - \int d\vec{r} \rho(\vec{r}) v_2(\vec{r}) = \int d\vec{r} \rho(\vec{r}) [v_1(\vec{r}) - v_2(\vec{r})] \text{ giving:}$$

$$E_2 + \int d\vec{r} \rho(\vec{r}) [v_1(\vec{r}) - v_2(\vec{r})] > E_1$$

However, working through the whole process again by expanding $\hat{H}_2 = \hat{H}_1 + [\hat{H}_2 - \hat{H}_1]$ leads to the result:

$$E_1 + \int d\vec{r} \rho(\vec{r}) [v_2(\vec{r}) - v_1(\vec{r})] > E_2$$

Adding these two equations leads to a cancellation of the integral terms and result in the contradiction $E_1 + E_2 > E_1 + E_2!$

Obviously the initial inequality is incorrect, and therefore there cannot be two different Hamiltonians that give the same density,

³ P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Physical Review* 136 (3B): B864–B871, 1964
http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1998/

and thus the assertion of HK1, that the density uniquely defines the Hamiltonian, is shown to be correct. The exact ground state energy E_0 is thus uniquely defined by the exact ground state density:

$E_0 = E[\rho]$ where E is the energy functional (a functional operates on a function)

The Second Hohenberg-Kohn Theorem (HK2) states that the energy functional is variational. To show this consider another density $\tilde{\rho}$ that determines its own wavefunction $\tilde{\Psi} \rightarrow \tilde{\rho}$

$$E[\tilde{\rho}] = \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle \geq \langle \Psi | \hat{H} | \Psi \rangle = E_0 = E[\rho]$$

The energy functional is thus variational, since $E[\tilde{\rho}] \geq E[\rho]$. The ground state energy can be determined from the density in a variational way

The energy, expressed as a functional of the density, can be divided into a system dependent part (the nuclear potential term) and a universal part, that describes everything else - it is universal in the sense that the operators are the same for any N -electron system:

$$E[\rho] = \int d\vec{r} \rho(\vec{r}) v_{nuc}(\vec{r}) + F_{HK}[\rho]$$

This functional attains its minimum value with respect to all allowed densities when the input density is equal to the true ground state density. As with Hartree-Fock calculations, the ground state density is the one which minimizes the energy - all we need to know is the form of the universal functional F_{HK} .

Kohn-Sham Theory

The Hohenberg-Kohn theorems establish that the density uniquely describes the system, and that the energy functional is variational, but we don't yet know what form F_{HK} takes.

However, at least the nuclear potential $\int d\vec{r} \rho(\vec{r}) v_{nuc}(\vec{r})$ is known (and is system specific)

The approach in Kohn-Sham (KS) theory⁴ is to expand the F_{HK} part of the energy functional into its individual terms. Ideally, the larger terms can be computed (nearly) exactly, and unknown errors can be restricted to the smaller terms. Expanding out the HK energy functional into kinetic energy, the interelectronic term and the nuclear potential:

$$E[\rho] = T[\rho] + V_{ee}[\rho] + \int d\vec{r} \rho(\vec{r}) v_{nuc}(\vec{r})$$

$$E[\rho] = T[\rho] + J[\rho] + E'_{xc}[\rho] + \int d\vec{r} \rho(\vec{r}) v_{nuc}(\vec{r})$$

Where $J[\rho]$ is known exactly (the Coulombic interaction term), while we have not yet established the other terms:

⁴ W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Physical Review* 140 (4A): A1133-A1138, 1965

$T[\rho]$ is a kinetic energy term; E'_{xc} contains everything else (exchange and correlation terms)

To compute the first term, the kinetic energy in Kohn-Sham theory, recall that we have defined already the kinetic energy of N non-interacting electrons in the HF approach:

$$T_{HF} = -\frac{1}{2} \sum_i \langle \chi_i | \nabla^2 | \chi_i \rangle$$

The exact wavefunction of non-interacting fermions is a Slater determinant; To solve the problem of defining the kinetic energy term, the KS approach is to set up a non interacting reference system represented by a Slater determinant. The orbitals are known as Kohn-Sham orbitals. Their physical meaning has been debated. There is always at least one Slater determinant such that $\Psi_{SD} \rightarrow \rho$ and the density can be extracted from the wavefunction:

$$\rho(\vec{r}) = \sum_{occupied} |\psi_i(\vec{r})|^2$$

We can use Ψ_{SD} to give most of the kinetic energy (i.e. of a fictitious system of non-interacting electrons which yields the same ground state density as the fully interacting system)

$$T[\rho] = T_s + T_c[\rho] \text{ where } T_s \text{ is defined as in HF: } T_s = -\frac{1}{2} \sum_{occupied} \langle \chi_i | \nabla^2 | \chi_i \rangle$$

Where $T_c[\rho]$ is the difference between the true KE, and that described by Ψ_{SD} So, the Kohn-Sham energy functional is now given by:

$$E_{KS} = T_s + T_c[\rho] + J[\rho] + E'_{xc}[\rho] + \int d\vec{r} \rho(\vec{r}) v_{nuc}(\vec{r})$$

We collect together the unknown $T_c[\rho]$ and $E'_{xc}[\rho]$ terms as $E_{xc}[\rho]$ Thus, the exchange correlation functional needs to include a correction to the kinetic energy. This formulation is still exact, however, the actual form of E_{xc} is not known.

Obtaining the Kohn-Sham Orbitals

We require to minimize E_{KS} in terms of the KS-orbitals that comprise Ψ_{SD} while ensuring that the orbital form an orthonormal set

$$\frac{\delta E_{KS}}{\delta \psi_i} = 0 \text{ subject to } \langle \psi_i | \psi_j \rangle = \delta_{ij}$$

Considering the individual terms of the functional separately, the kinetic energy term:

$$T_s = -\frac{1}{2} \sum_{occ.} \langle \psi_j | \nabla^2 | \psi_j \rangle = -\frac{1}{2} \int d\vec{r} (\sum_{occ.} \psi_j \nabla^2 \psi_j)(\vec{r})$$

$$\frac{\delta T_s}{\delta \psi_i} = -\nabla^2 \psi_i$$

Nuclear potential energy term (using the chain rule):

$$\begin{aligned}
\frac{\delta}{\delta\psi_i} \int d\vec{r} v_{nuc} \rho(\vec{r}) &= \frac{\delta\rho}{\delta\psi_i} \frac{\delta}{\delta\rho} \int d\vec{r} v_{nuc} \rho(\vec{r}) \\
&= 2\psi_i \frac{\delta}{\delta\rho} \int d\vec{r} v_{nuc} \rho(\vec{r}) \text{ since } \rho(\vec{r}) = \sum_{occupied} |\psi_i(\vec{r})|^2 \\
&= 2\psi_i v_{nuc}
\end{aligned}$$

Coulombic energy term:

$$J[\rho] = \frac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} = \frac{1}{2} \int d\vec{r}_1 \rho(\vec{r}_1) v_j(\vec{r}_1)$$

$$\text{where } v_j(\vec{r}_1) = \int d\vec{r}_2 \frac{\rho(\vec{r}_2)}{r_{12}}$$

$$\frac{\delta J[\rho]}{\delta\rho} = \frac{\delta}{\delta\rho} \frac{1}{2} \int d\vec{r}_1 \rho(\vec{r}) v_j(\vec{r}) = v_J$$

$$\text{Using the chain rule as above } \frac{\delta J[\rho]}{\delta\psi_i} = 2\psi_i \frac{\delta J[\rho]}{\delta\rho} = 2\psi_i v_J$$

Exchange-Correlation term:

$$\frac{\delta E_{XC}[\rho]}{\delta\psi_i} = 2\psi_i \frac{\delta E_{XC}[\rho]}{\delta\rho} \text{ (chain rule)}$$

defining the exchange-correlation potential:

$$v_{XC} = \frac{\delta E_{XC}[\rho]}{\delta\rho}$$

$$\frac{\delta E_{XC}[\rho]}{\delta\psi_i} = 2\psi_i v_{XC}$$

Collecting the above terms together and setting equal to zero subject to the constraint that $\langle\psi_i|\psi_j\rangle = \delta_{ij}$ leads to the set of Kohn-Sham equations:

$$[-\frac{1}{2}\nabla^2 + v_{nuc} + v_J + v_{XC}]\psi_i = \epsilon_i\psi_i$$

Compare with the Hartree-Fock equations:

$$[-\frac{1}{2}\nabla^2 + v_{nuc} + v_J - \hat{K}]\psi_i = \epsilon_i\psi_i$$

The Kohn-Sham equations describe n non-interacting particles moving in an effective potential. All we need to do now is to define the form of v_{XC} - although there are several hundred (thousands?) of forms (the functional zoo)...

Lecture 2. Implementations of Density Functional Theory

A brief recap of the Hohenberg-Kohn theorems and Kohn-Sham DFT:

HK 1: The exact ground state energy E_0 is uniquely defined by the exact ground state density ρ_0 $E_0 = E[\rho]$, where E is the energy functional (a functional operates on a function)

HK 2: The energy functional is variational, $E[\tilde{\rho}] \geq E[\rho]$ - the ground state energy can be determined from the density in a variational way

$$E_{KS} = T_s + T_c[\rho] + J[\rho] + E'_{xc}[\rho] + \int d\vec{r} \rho(\vec{r}) v_{nuc}(\vec{r})$$

$$T_s = -\frac{1}{2} \sum_{occ.} \langle \psi_j | \nabla^2 | \psi_j \rangle = -\frac{1}{2} \int d\vec{r} (\sum_{occ.} \psi_j \nabla^2 \psi_j)(\vec{r})$$

$$[-\frac{1}{2} \nabla^2 + v_{nuc} + v_J + v_{XC}] \psi_i = \epsilon_i \psi_i$$

Now let's look at some possible forms for v_{XC} . Remembering that the potential $v_{XC} = \frac{\delta E_{XC}[\rho]}{\delta \rho}$ we can focus on the form of E_{XC} .

E_{XC} contains contributions from electronic exchange and correlation (dynamic - remember that a single determinant fails for left-right correlation). We will separate these contributions.

The Uniform Electron Gas (UEG)

The UEG is a useful model since the density (as the name would suggest) is constant across space. This is quite unlike molecules, where greater density lies around the nuclei. Also called the jellium model, nuclei are replaced by a uniform background positive charge - the electrons move in this medium.

Arguably, the UEG is a model for e.g. sodium metal. More importantly, however, it is the only system for which we know the form of the exchange and correlation energy exactly or to very high accuracy.

Central to this model is the local density approximation, LDA, which means that we can write:

$$E_{XC}^{LDA}[\rho] = \int \rho(\vec{r}) \epsilon_{XC}(\rho(\vec{r})) d\vec{r}$$

i.e. the value of the exchange-correlation energy at a point in space depends on the density at that point alone, $\rho(\vec{r})$, and is weighted by the probability that there is an electron at that point

Separating into the contributions from exchange and correlation

$$\epsilon_{XC}(\rho(\vec{r})) = \epsilon_X(\rho(\vec{r})) + \epsilon_C(\rho(\vec{r}))$$

The exchange part in a uniform electron gas was originally derived by Bloch and Dirac, but is also equivalent to that used by Slater in the approximation of HF exchange:

$$\epsilon_X = -\frac{3}{4} \sqrt{\frac{3\rho(\vec{r})}{\pi}}$$

$$\text{so that } E_X^{\text{Slater}} = -\frac{3}{4}\sqrt{\frac{3}{\pi}} \int \rho^{\frac{4}{3}}(\vec{r}) d\vec{r}$$

Since for the UEG, the density is constant, $E_X^{\text{UEG}} = -0.7386V\rho^{\frac{4}{3}}$

Can we justify the exponent in terms of dimensional analysis?

$\int \rho(\vec{r}) d\vec{r}$ is dimensionless, so $\int \rho^{\frac{4}{3}}(\vec{r}) d\vec{r}$ has units of inverse length.

In general, we could apply this approach to a non-uniform density by carrying out the integration of $\int \rho^{\frac{4}{3}}(\vec{r}) d\vec{r}$

For the UEG, the potential is therefore given by $v_x^S(\vec{r}) = \frac{\delta E_X^S[\rho]}{\delta \rho} = -\frac{4}{3} \cdot 0.7386 \cdot \rho^{\frac{1}{3}}$

This exchange functional is referred to as Slater exchange, abbreviated as S.

No such explicit expression is known for the correlation part and so the standard approach is to fit to high accuracy quantum Monte-Carlo (QMC) simulations of the homogeneous electron gas - analytical expressions have been derived from interpolation. Popular forms are described by Vosko, Wilk and Nusair (VWN)⁵ and Perdew and Wang (PW).⁶

The generalized gradient approximation (GGA)

So far we have considered a local functional where the exchange energy evaluated at a given point depends only the value of the density at that point in space.

The gradient of the density gives some additional "non-local" information - i.e. it's the first term of a Taylor expansion about a particular point.

However, mathematically speaking, the inclusion of the gradient will still give rise to a local functional (semi-local) - the value will remain independent of other points (unlike HF exchange).

A gradient-corrected functional can be constructed to account for the inhomogeneity of true electron density.⁷

$$F[\rho] = \int d\vec{r} f(\rho(\vec{r}), |\nabla\rho|(\vec{r}))$$

$|\nabla\rho|$ is the gradient of the density, but it's more convenient to make this quantity dimensionless, $s(\vec{r}) = \frac{|\nabla\rho|(\vec{r})}{\rho^{\frac{4}{3}}(\vec{r})}$

We can write the exchange energy in terms of the Slater expression and a correction associated with the local non-uniformity of the density:

$$E_X^{\text{GGA}} = E_X^{\text{LDA}} - \int F(s(\vec{r}))\rho^{\frac{4}{3}}(\vec{r}) d\vec{r}$$

For a UEG the second term vanishes as $s(\vec{r})$ is zero everywhere. Division by the density means that in a molecule this value of s (the local

⁵ S. H. Vosko, L. Wilk, and M. Nusair. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis. *Can. J. Phys.*, 58, 1200-11, 1980

⁶ J. P. Perdew, K. Burke, and Y. Wang. Generalized gradient approximation for the exchange-correlation hole of a many-electron system. *Phys. Rev. B*, 54, 16533-39., 1996

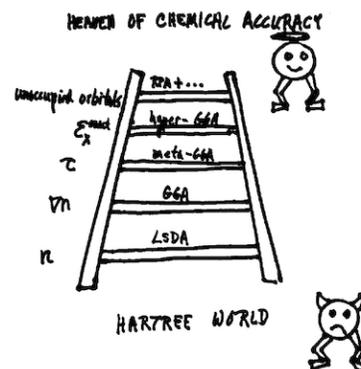


Figure 2: Jacob's ladder of density functionals ascending to chemical accuracy. From ref. 7

⁷ J. P. Perdew, A. Ruzsinszky, L. A. Constantin, J. Sun, and G. I. Csonka. Some fundamental issues in ground-state density functional theory: A guide for the perplexed. *J. Chem. Theory Comput.* 5 (4), 902-908, 2009

inhomogeneity parameter) is large for large gradients but also small densities and vice-versa.

One of the most well-used forms of the function F is given by Becke in 1988⁸:

$$F^{B88} = \frac{\beta s^2}{1 + 6\beta s \cdot \sinh^{-1}(s)}$$

The empirical parameter β was fit to exactly known exchange energies of the noble gas atoms as 0.0042

(GGA) Generalised Gradient Approximation functionals evaluate $|\nabla\rho|$ - the higher derivative of the density, $|\nabla^2\rho|$, is used in meta-GGA functionals (e.g. Tao, Perdew, Staroverov, and Scuseria - TPSS)

Correlation functionals

No simple physical motivation for the form of correlation functionals. Interpolation of high accuracy wavefunction based results obtained for the UEG. Lee-Yang-Parr (LYP) is based on the correlation energy of the Helium atom and contains one parameter.

$$\begin{aligned} f = & -4A\rho(a)\rho(b)\left(1 + \frac{d}{\sqrt{\rho}}\right)^{-1}\rho^{-1} \\ & - AB\omega\left(\rho(a)\rho(b)\left(82^{2/3}cf((\rho(a))^{8/3} + (\rho(b))^{8/3}) + \left(\frac{47}{18} - \frac{7}{18}\delta\right)\sigma\right.\right. \\ & \left.\left. - (5/2 - 1/18\delta)(\sigma(aa) + \sigma(bb)) - 1/9(\delta - 11)\left(\frac{\rho(a)\sigma(aa)}{\rho} + \frac{\rho(b)\sigma(bb)}{\rho}\right)\right)\right) \\ & - 2/3\rho^2\sigma + (2/3\rho^2 - (\rho(a))^2)\sigma(bb) + (2/3\rho^2 - (\rho(b))^2)\sigma(aa), \end{aligned} \quad (84)$$

⁸ A. D. Becke. Density-functional exchange-energy approximation with correct asymptotic-behavior. *Phys. Rev. A*, 38, 3098-100., 1988

Figure 3: Lee-Yang-Parr correlation functional

Hybrid functionals

E_{XC} as defined in KS theory has to contain the difference between the kinetic energy of the real, fully interacting system and that of the non-interacting reference system. To do this, imagine that the two systems central to KS (the non-interacting reference with no electron-electron interaction, and the real system) are connected by gradually increasing the coupling strength parameter, λ from 0 to 1.

$$E_{XC} = \int_0^1 U_{XC}^\lambda d\lambda - \text{the adiabatic connection formula}$$

$\lambda = 0$ represents the non-interacting KS reference system, while $\lambda=1$ represents the fully interacting real system, and the two extremes are connected through a continuum of partially interacting systems sharing a common density. The λ integration generates the kinetic energy part.

We don't know the exact λ -dependence of E_{XC} - a simplifying assumption would be a linear transition between the HF and KS limits, in which case the integral simplifies to their average value. This is the approach of Becke's half and half functional, BHandH:

$$E_{XC} = \frac{1}{2}E_{XC}^{\lambda=0} + \frac{1}{2}E_{XC}^{\lambda=1} = \frac{1}{2}E_{XC}^{HF} + \frac{1}{2}E_{XC}^{SWVN}$$

The absolute average error for G2 atomization energies is 6.5 kcal/mol, and rivals the value of 5.7 kcal/mol for the gradient-corrected BPW91, if basis-set free, fully numerical results are utilized. (the G2 data-set includes small molecules consisting of first- and second-row atoms)

Coefficient a reflects the relative importance of a system's independent-particle character, or, equivalently, the rate of onset of correlation as λ increases from zero.

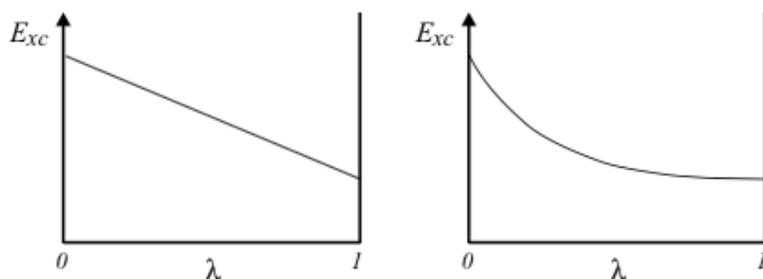


Figure 4: λ dependence of E_{XC} from exact exchange at 0 to KS exchange-correlation at 1. From ref. 1.

These parameters are obtained by minimising the error of small molecule atomization energies, ionisation potentials and proton affinities with respect to composite ab initio calculations.

Becke's empirically-determined three-parameter hybrid⁹ mixes HF and local (Slater) exchange in the ratio of 20:80, and includes a contribution from the gradient-corrected B88 (discussed above):

$$\text{B3LYP: } E_{XC} = E_{XC}^{LSD} + a(E_{XC}^{HF} - E_X^{LSD}) + bE_X^{B88} + cE_C^{LYP} + (1 - c)E_C^{VWN}$$

where $a = 0.20$, $b = 0.72$ and $c = 0.81$

This three-parameter fit reduced the average absolute error in the G2 atomization energies to 2 kcal/mol. Becke's 1993 paper has around 58,000 citations at the beginning of 2015.

So called hybrid GGA functionals, such as B3LYP, incorporating exact exchange and the density gradient, have been the mainstay of computations for small organic and inorganic molecules for over a decade. However, long range correlation is not described well even by a semi-local functional, leading to severe underestimation (or neglect) of dispersion interactions. The HF exchange is non-local but dispersion is inherently associated with correlation.

⁹ A. D. Becke. Density-functional thermochemistry. iii. the role of exact exchange. *J. Chem. Phys.*, 98, 5648-52., 1993

TD-DFT

So far we have discussed the ground-state electron density, but DFT can be extended to treatment of excited states, for example by considering the linear response of the density to weak perturbations. Excited states result when a molecule interacts with an oscillating (i.e. time-dependent) electric field. The time-dependent Schrodinger equation:

$$i \frac{\delta}{\delta t} \psi(t) = \hat{H} \psi(t)$$

Analogously to the Hohenberg-Kohn theorem, for time-dependent problems we use the Runge-Gross theorem¹⁰: For a given initial state, a one-to-one correspondence exists between the time-dependent density $\rho(r, t)$ and the time-dependent external potential $v_{ext}(r, t)$.

Time-dependent Kohn-Sham equations map the problem of interacting electrons moving in a time-dependent external potential v_{ext} onto a system of independent electrons moving in a time-dependent effective potential v_{eff}

$$i \frac{\delta}{\delta t} \psi(\vec{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff}[\rho(\vec{r}, t)] \right] \psi(\vec{r}, t)$$

If we can assume a weak external perturbation, (i.e. no lasers!) then the change in the density can be assumed to be linearly dependent on the perturbation:

$$\delta\rho(\vec{r}, t) = \int dt' \int d^3\vec{r}' \chi(\vec{r}, \vec{r}', t - t') \delta v_{ext}(\vec{r}', t')$$

The linear response function $\chi(\vec{r}, \vec{r}', t - t')$ describes the change in the density at \vec{r}, t when the external potential undergoes a small change at \vec{r}', t'

$$\chi(\vec{r}_1 t_1, \vec{r}_2 t_2) = \chi_{KS}(\vec{r}_1 t_1, \vec{r}_2 t_2) + \chi_{KS}(\vec{r}_1 t_1, \vec{r}_2 t_2) \left(\frac{1}{|\vec{r}_2 - \vec{r}_1|} + f_{xc}(\vec{r}_2 t_2, \vec{r}_1 t_1) \right) \chi(\vec{r}_1 t_1, \vec{r}_2 t_2)$$

The problem of finding excitation energies of the interacting system is mapped into the search for the poles of the response function.

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¹⁰ E. Runge and E. K. U. Gross. Density-functional theory for time-dependent systems. *Phys. Rev. Lett.* 52 (12): 997-1000, 1984

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