

Density Functional Theory

Shouldn't things be simpler than dealing with a wave function for a many-electron system? Rather than working with a wave function, which has rather odd units of probability density to the one-half power, why can't we work with some physical observable in determining the energy (and possibly other properties) of a molecule? What observable we should choose then?

The Hamiltonian depends only on the positions and atomic numbers of the nuclei and the total number of electrons. The dependence on total number of electrons immediately suggests that a useful physical observable would be the electron density ρ , because, integrated over all space, it gives the total number of electrons:

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

Because the nuclei are effectively point charges, their positions correspond to local maxima in the electron density and these maxima are also cusps. For each nucleus A located at an

electron density maxima \mathbf{r}_A

$$\left. \frac{\partial \bar{\rho}(r_A)}{\partial r_A} \right|_{r_A=0} = -2Z_A \rho(r_A)$$

Z – the atomic number of A, r_A – the radial distance from A

$\bar{\rho}$ – the spherically averaged electron density

Therefore, given a known density, one could form a Hamiltonian operator, solve the Schrödinger equation, and determine the wave functions and energy eigenvalues:

Density contains all the information we need!

The Hohenberg-Kohn Existence Theorem

In the language of density functional theory (DFT), electrons interact with one another and with an external potential. In the uniform electron gas, the external potential is the uniformly distributed positive charge, and in a molecule, the external potential is the attraction to the nuclei. To establish a dependence of the energy on the density it is sufficient to show that this density determines the Hamiltonian operator. Also, integration of the density gives the number of electrons, so we need to determine the external potential (the charges and positions of the nuclei). The Hohenberg-Kohn theorem states that the Hamiltonian operator (and therefore, the energy) can be uniquely determined from the ground state density. We can prove this theorem via *reductio ad absurdum*, that is, we show that an assumption to the contrary generates an impossible result.

Let's assume that two different external potentials can each be consistent with the same ground-state density ρ_0 . We will call these two potentials v_a and v_b and the corresponding different Hamiltonian operators will be H_a and H_b . With each Hamiltonian will be associated a ground-state wave function Ψ_0 and its associated eigenvalue E_0 . The variational theorem of MO theory states that the expectation value of the Hamiltonian a over the wave function b must be higher than the ground-state energy of a :

$$E_{0,a} < \langle \Psi_{0,b} | H_a | \Psi_{0,b} \rangle$$

We can rewrite this expression as

$$E_{0,a} < \langle \Psi_{0,b} | H_a - H_b + H_b | \Psi_{0,b} \rangle < \langle \Psi_{0,b} | H_a - H_b | \Psi_{0,b} \rangle + \langle \Psi_{0,b} | H_b | \Psi_{0,b} \rangle < \langle \Psi_{0,b} | v_a - v_b | \Psi_{0,b} \rangle + E_{0,b}$$

The potentials v are one-electron operators, therefore, the integral can be written in terms of the ground state density

$$E_{0,a} < \int [v_a(r) - v_b(r)]\rho_0(r)dr + E_{0,b}$$

If we interchange a and b , we can also write

$$E_{0,b} < \int [v_b(r) - v_a(r)]\rho_0(r)dr + E_{0,a}$$

If we add the two inequalities together, we have

$$\begin{aligned} E_{0,a} + E_{0,b} &< \int [v_a(r) - v_b(r)]\rho_0(r)dr + \int [v_b(r) - v_a(r)]\rho_0(r)dr + E_{0,b} + E_{0,a} \\ &< \int [v_a(r) - v_b(r) + v_b(r) - v_a(r)]\rho_0(r)dr + E_{0,b} + E_{0,a} < E_{0,a} + E_{0,b} \end{aligned}$$

We are left with an impossible result, which must indicate that our initial assumption was incorrect. So, the ground-state density must determine the external potential, and thus the Hamiltonian, and thus the wave function. The Hamiltonian determines not just the ground-state wave function, but all excited state wave functions as well – a tremendous amount of information is coded in the density.

The Hohenberg-Kohn Variational Theorem

The existence theorem does not show us how to predict the density of the system.

Hohenberg and Kohn showed in a second theorem that, also just as with MO theory, the density obeys the variational principle.

Let's assume we have some well-behaved candidate density that integrates to the proper number of electrons, N . In that case, the first theorem indicates that this density determines a candidate wave function and Hamiltonian. Then, we can evaluate the energy expectation value

$$\langle \Psi_{cand} | H_{cand} | \Psi_{cand} \rangle = E_{cand} \geq E_0$$

So, in principle, we can keep choosing different densities and those that provide lower energies are closer to correct. However, at this stage, first, we have no prescription for how to choose improved density candidates rationally, and second, as the motivation for DFT was to avoid solving the Schrödinger equation, computing the energy as the expectation value of the Hamiltonian is no advance – we know how to do that already.

The difficulty lies in the nature of the functional itself. We know that, in principle, from the density we can find the Hamiltonian, and the wave function, and hence the energy, but we do not actually how to do that. What we actually want is to determine the energy directly from density.

Kohn-Sham self-consistent field method

Kohn and Sham (1965) realized that the consideration can be simplified if only the Hamiltonian operator were one for a non-interacting system of electrons. Such a Hamiltonian can be expressed as a sum of one-electron operators, has eigenfunctions that are Slater determinants of the individual one-electron eigenfunctions, and has eigenvalues that are simply the sum of the one-electron eigenvalues. Kohn and Sham's idea – to take as a starting point a fictitious system of non-interacting electrons that have for their overall ground-state density the same density as some real system of interest where the electrons do interact. Since the density determines the position and atomic numbers of the nuclei, these quantities are necessarily identical in the non-interacting and in the real systems.

Next, we divide the energy functional into specific components:

$$E[\rho(r)] = T_{ni}[\rho(r)] + V_{ne}[\rho(r)] + V_{ee}[\rho(r)] + \Delta T[\rho(r)] + \Delta V_{ee}[\rho(r)]$$

The terms in the above expression refer, respectively, to the kinetic energy of the non-interacting electrons, the nuclear-electron interaction, the classical electron-electron repulsion, the correction to the kinetic energy deriving from the interacting nature of the electrons, and all non-classical corrections to the electron-electron repulsion energy. For a non-interacting system of electrons, the kinetic energy is just the sum of the individual electronic kinetic energies. If we express density in terms of orbitals, we can rewrite the expression as

$$E[\rho(r)] = \sum_i^N \left(\langle \chi_i | -\frac{1}{2} \nabla_i^2 | \chi_i \rangle - \langle \chi_i | \sum_k^{\text{nuclei}} \frac{Z_k}{|r_i - r_k|} | \chi_i \rangle \right) + \sum_i^N \langle \chi_i | \frac{1}{2} \int \frac{\rho(r')}{|r_i - r'|} dr' | \chi_i \rangle + E_{xc}[\rho(r)]$$

N – the number of electrons. We have used that the density for a Slater-determinantal wave function (which is an exact eigenfunction for the non-interacting system) is simply

$$\rho = \sum_{i=1}^N \langle \chi_i | \chi_i \rangle$$

The difficult terms ΔT and ΔV_{ee} have been collected together in a term E_{xc} – the exchange-correlation energy. The term includes not only the effects of quantum mechanical exchange and correlation, but also the correction for the classical self-interaction energy and for the difference in kinetic energy between the fictitious non-interacting system and the real one.

Now, if we want to find the orbitals χ that minimize E (the variational principle), they satisfy the equations:

$$h_i^{KS} \chi_i = \varepsilon_i \chi_i$$

The Kohn-Sham (KS) one-electron operator is defined as

$$h_i^{KS} = -\frac{1}{2} \nabla_i^2 - \sum_k^{nuclei} \frac{Z_k}{|r_i - r_k|} + \int \frac{\rho(r')}{|r_i - r'|} dr' + V_{xc}$$

$$V_{xc} = \frac{\delta E_{xc}}{\delta \rho} \text{ - functional derivative}$$

Because the E that we are minimizing is exact, the orbitals χ must provide the exact density: the minimum must correspond to reality. It is these orbitals that form the Slater-determinantal eigenfunction for the separable non-interacting Hamiltonian defined as the sum of the Kohn-

Sham operators,

$$\sum_{i=1}^N h_i^{KS} |\chi_1 \chi_2 \cdots \chi_N\rangle = \sum_{i=1}^N \varepsilon_i |\chi_1 \chi_2 \cdots \chi_N\rangle,$$

so there is internal consistency in the Kohn-Sham approach of positing a non-interacting system with a density identical to that for the real system.

To determine the KS orbitals, we express them within a basis set of functions $\{\phi\}$ and then determine the individual orbital coefficients by solution of a secular equation analogous to that employed for HF theory, except the Fock matrix elements $F_{\mu\nu}$ are replaced by elements $K_{\mu\nu}$ defined by

$$K_{\mu\nu} = \langle \phi_\mu | -\frac{1}{2} \nabla^2 - \sum_k^{nuclei} \frac{Z_k}{|r - r_k|} + \int \frac{\rho(r')}{|r - r'|} dr' + V_{xc} | \phi_\nu \rangle$$

The kinetic energy and nuclear attraction components of matrix elements of \mathbf{K} are identical to those for \mathbf{F} . If the density appearing in the classical interelectronic repulsion component is expressed in the same basis functions used for the Kohn-Sham orbitals, then the result is that the same two-electron electron repulsion integrals appear in \mathbf{K} as are found in \mathbf{F} – it is simple to modify existing codes for HF calculations to also perform DFT computations. As the density is required for computation of the secular matrix elements, but the density is determined using the orbitals derived from solution of the secular equation, the Kohn-Sham process must be carried out as an iterative SCF procedure.

There is a key difference between HF theory and DFT – DFT contains no approximations: it is exact. All we need to know is E_{xc} as a function of ρ . Unfortunately, while Hohenberg and Kohn proved that a functional of the density must exist, their proofs provide no guidance whatsoever what it is – considerable research effort continues to find functions of the density that may be expected to reasonably approximate E_{xc} . The key contrast between HF and DFT (in the limit of an infinite basis set) – HF is a deliberately approximate theory, whose development was in part motivated by an ability to solve the relevant equations exactly, while DFT is an exact theory, but the relevant equations must be solved approximately because a key operator has unknown form. Also, although exact DFT is variational, this is not true once approximations for E_{xc} are adopted.

Exchange-correlation functionals

In principle E_{xc} not only accounts for the difference between the classical and quantum mechanical electron-electron repulsion, but it also includes the difference in kinetic energy between the fictitious non-interacting system and the real system. In practice, most modern functionals do not attempt to compute this portion explicitly. In many functionals, empirical parameters appear, which introduce some kinetic energy correction if they are based on experiment.

The functional dependence of E_{xc} on the electron density is expressed as an interaction between the electron density and an 'energy density' ε_{xc} that is dependent on the electron density:

$$E_{xc}[\rho(r)] = \int \rho(r) \varepsilon_{xc}[\rho(r)] dr$$

The energy density ε_{xc} is always treated as a sum of individual exchange and correlation contributions. The simplest system, for which one can derive the exchange and correlation energy density is the uniform electron gas. Slater had derived the exchange energy density for it as

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

Local density approximation

The term local density approximation (LDA) was originally used to indicate any density functional theory where the value of ε_{xc} at some position \mathbf{r} could be computed exclusively from the value of ρ at that position, i.e., the ‘local’ value of ρ .

For the correlation energy density, even for the ‘simple’ uniform electron gas no analytical derivation of this functional has proven possible. However, using quantum Monte Carlo techniques, Ceperley and Alder (1980) computed the total energy for electron gases for several different densities to very high numerical accuracy. By subtracting analytical exchange for each case, they were able to determine the correlation energy in these systems. Vosko, Wilk, and Nusair (1980) later designed local functionals of the density fitting to these results:

$$\varepsilon_c^i(r_s) = \frac{A}{2} \left\{ \ln \frac{r_s}{r_s + b\sqrt{r_s} + c} + \frac{2b}{\sqrt{4c - b^2}} \tan^{-1} \left(\frac{\sqrt{4c - b^2}}{2\sqrt{r_s} + b} \right) - \frac{bx_0}{x_0^2 + bx_0 + c} \left\{ \ln \left[\frac{(\sqrt{r_s} - x_0)^2}{r_s + b\sqrt{r_s} + c} \right] + \frac{2(b + 2x_0)}{\sqrt{4c - b^2}} \tan^{-1} \left(\frac{\sqrt{4c - b^2}}{2\sqrt{r_s} + b} \right) \right\} \right\}$$

Here, r_s is called effective radius – exactly one electron would be contained within the sphere defined by that radius if this sphere have the same density throughout:

$$r_s(\rho) = \left(\frac{3}{4\pi\rho(r)} \right)^{1/3}$$

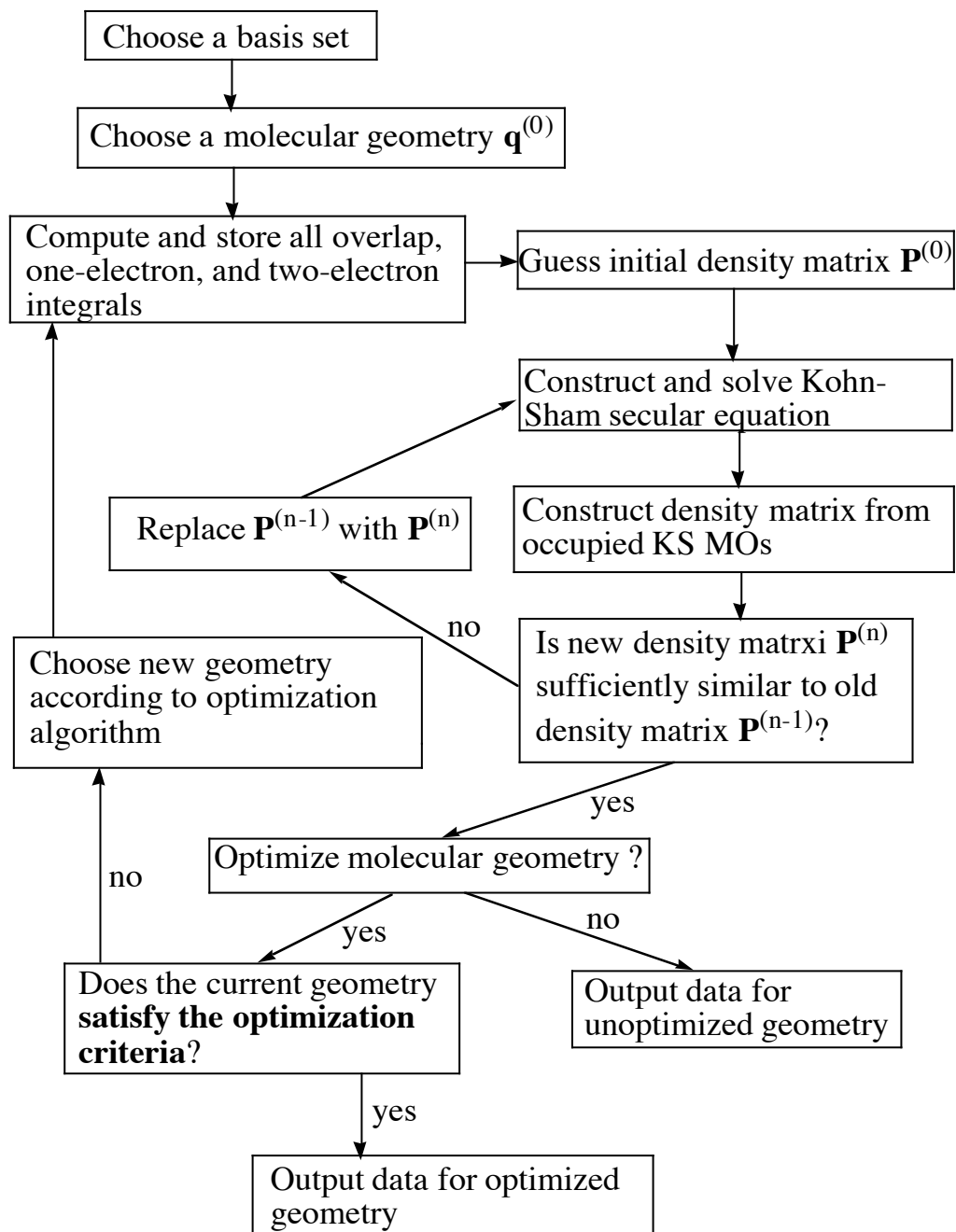
Different sets of empirical constants A , x_0 , b , and c are used for $i = 0$ and $i = 1$. LDA (sometimes called LSDA – local spin density approximation) calculations that employ a combination of Slater exchange and VWN correlation energy expression are referred to as SVWN.

It is apparent how complex the correlation energy functional in a completely general system may be expected to be. Most modern DFT approaches can be described as semiempirical methods because they include empirically optimized constants and functional forms. Solution of the integrals employing the VWN correlation functional is highly unlikely to be accomplished analytically.

The steps involved in a LSDA calculation (see the flow chart on the next page) are for the most part similar to those for a HF calculation. After choice of molecular geometry, the overlap integrals and the kinetic energy and nuclear attraction integrals are computed. To evaluate the remaining integrals, we must guess an initial density, and this density can be constructed as a matrix equivalent to the density matrix used in HF theory. With our guess density in hand, we can construct V_{xc} and evaluate the remaining integrals in each KS matrix element. After this point, the KS and HF SCF schemes are essentially identical. Once convergence of the SCF is achieved, the energy is computed by plugging the final density into

$$E[\rho(r)] = T_{ni}[\rho(r)] + V_{ne}[\rho(r)] + V_{ee}[\rho(r)] + \Delta T[\rho(r)] + \Delta V_{ee}[\rho(r)]$$

This is in contrast to HF theory, where the energy is evaluated as the expectation value of the Hamiltonian operator acting on the HF Slater determinant.



Flow chart of the KS SCF procedure

Density gradient corrections

How to best represent the exchange-correlation functional? We start with the LSDA approximation applied to a molecule. Invoking the uniform electron gas as the source of the energy expressions is not equivalent to the assumption that the electron density of the molecule is a constant throughout the space. Instead, it is an assumption that the exchange-correlation energy density at every position of space for the molecule is the same as it would be for the uniform gas having the same density as is found at that position.

In a molecular system, the electron density is typically rather far from uniform – the LDA approach will have limitations. One way to improve the correlation potential – to make it depend not only on the local value of the density, but on the extent to which the density is locally changing – the gradient of the density – ‘non-local’ DFT or ‘gradient-corrected’ DFT – the generalized gradient approximation’ (GGA). Most gradient-corrected functionals are constructed by adding a correction term to the LDA functional:

$$\varepsilon_{x/c}^{GGA}[\rho(r)] = \varepsilon_{x/c}^{LDA}[\rho(r)] + \Delta\varepsilon_{x/c} \left[\frac{|\nabla\rho(r)|}{\rho^{4/3}(r)} \right]$$

The most popular GGA exchange functional – Becke (1988), ‘B’. It has correct asymptotic behavior at long range for the energy density and incorporates a single empirical parameter the value of which is optimized by fitting to the exactly known exchange energies of the six noble gas atoms He-Rn. Alternative GGA exchange functionals have been also developed, but most of them have seen little use in the wider literature in comparison to B, besides, probably, the PW exchange functional (Burke, Perdew, and Wang 1998).

Correlation functionals: corrections to the correlation energy density with respect to its LDA value include P86 (Perdew 1986), PW91 (Perdew and Wang 1992, Perdew et al. 1992), and B95 (Becke 1996). The P86 functional includes one empirical parameter fitted for the neon atom. The PW91 and B95 functionals contain no empirical parameters. Arguably, the most popular correlation functional, LYP, does not correct the LDA expression but computes the full correlation energy (Lee, Yang, and Parr 1988). It contains four empirical parameters fit to the helium atom. LYP is the only functional that provides an exact cancellation of the self-interaction error in one-electron system.

Typically in the literature, a complete specification of the exchange and correlation functionals is accomplished by concatenating the two acronyms in that order: acronym for the exchange functional first followed by the acronym for the correlation functional: BLYP, BP86, BPW91, etc.

Another useful idea is to combine the exchange-correlation functional with the exact exchange that can be obtained from Hartree-Fock calculations:

$$E_{xc} = (1 - a)E_{xc}^{DFT} + aE_x^{HF}$$

If $a = 0.5$ – ‘half-and-half’ (H&H) method. Using LDA exchange-correlation, Becke (1993) showed that the H&H approach had an error of 6.5 kcal/mol over a subset of the G3 enthalpy of formation test (about 250 different molecules of the first and second row elements). This compared quite favorably with the GGA method BPW91, which had an error of 5.7 kcal/mol over the same set.

If one wants to estimate a constant like a , one might choose a value that maximizes the utility of the method. One may also include additional empirical parameters if this would result in sufficient improvement of accuracy.

Becke was the first to do this, developing the 3-parameter functional expression:

$$E_{xc}^{B3PW91} = (1-a)E_x^{LSDA} + aE_x^{HF} + b\Delta E_x^B + E_c^{LSDA} + c\Delta E_c^{PW91}$$

a , b , and c were optimized to 0.20, 0.72, and 0.81, respectively. The name of the functional, B3PW91, implies its use of a three-parameter scheme and the GGA exchange and correlation potentials B and PW91, respectively.

Stevens et al. (1994) modified this potential to use LYP instead of PW91. Because LYP is designed to compute the full correlation energy, and not a correction to LSDA, the B3LYP model is defined by

$$E_{xc}^{B3LYP} = (1-a)E_x^{LSDA} + aE_x^{HF} + b\Delta E_x^B + (1-c)E_c^{LSDA} + c\Delta E_c^{LYP}$$

a , b , and c have the same values as in B3PW91. Of all modern functionals, B3LYP is the most popular, its overall performance is remarkably good.

The methods which incorporate HF and DFT exchange are called hybrid DFT methods. Experience indicates that GGA functionals have certain systematic errors. For instance, they tend to underestimate barrier heights to chemical reactions. On the other hand, HF theory tends to overestimate barrier heights – one may regard the addition of HF exchange to ‘pure’ DFT results as a way to decrease the errors in barrier heights. Lynch et al. (2000) have reoptimized the percent HF exchange in the *m*PW1PW91 model against a database of energies of activation and reaction for hydrogen-atom transfer reactions – their model was called MPW1K (‘K’ for kinetics). MPW1K increases the percentage HF contribution in the functional by about a factor of 2 and leads to significantly improved performance over the chosen test set. Pople’s group proposed a parametrized pure GGA designed to give good results with small basis sets – EDF1, etc., etc., etc. ...

Advantages and disadvantages of DFT compared to MO theory

Since 1990 there has been an enormous amount of comparison between DFT and alternative methods based on the molecular wave function – as a rule, DFT is the most cost-effective method to achieve a given level of accuracy. There are, however, significant exceptions from this rule, deriving either from inadequacies in modern functionals or intrinsic limitations in the KS approach for determining the density.

Densities vs. wave functions

The most fundamental difference between DFT and MO theory – DFT optimizes an electron density while MO theory optimizes a wave function. To determine a particular molecular property using DFT, we need to know how that property depends on the density, while to determine the same property using a wave function, we need to know the correct quantum chemical operator. There are more well-characterized operators than generic property functionals of the density – wave functions clearly have broader utility. Example – the total energy of interelectronic repulsion. Even if we have the exact density for some systems, we do not know the exact exchange-correlation energy functional and cannot compute the exact interelectronic repulsion. However, with the exact wave function it is simple to evaluate the expectation value for the interelectronic repulsion operator to determine this energy:

$$E_{ee} = \langle \Psi | \sum_{i < j} \frac{1}{r_{ij}} | \Psi \rangle$$

Another example – the area of dynamics. Transition probabilities depend on matrix elements between different wave functions. Densities do not have phases as wave functions do – multistate resonance effects, interference effects, etc., are not readily computed by DFT. There is a DFT wave function; it is just not clear how useful it should be considered to be. The Slater determinant formed from the KS orbitals is the exact wave function for the fictional non-interacting system having the same density as the real system. This KS Slater determinant has certain interesting properties by comparison to its HF analogs. The shapes of KS orbitals tend to be similar to canonical HF MOs, and they can be quite useful in qualitative analysis of chemical properties. All KS orbitals, occupied and virtual, are subject to the same external potential. On the other hand, HF virtual orbitals experience the potential that would be felt by an extra electron being added to the molecule – HF virtual orbitals tend to be too high in energy and too diffuse compared to KS virtual orbitals. In exact DFT, it can be shown that the eigenvalue of the highest KS MO is the exact first ionization potential, a direct analogy to Koopmans' theorem for this orbital. However, in practice, approximate functionals are quite bad at predicting IPs.

Computational efficiency

The formal scaling behavior of DFT – N^3 , where N is the number of basis functions used to represent the KS orbitals. This is better than HF by a factor of N , and very much better than other methods including electron correlation.

An interesting possibility is the use of plane waves as basis sets in periodic infinite systems (metals, crystalline solids, or liquids represented using periodic boundary conditions). While it takes an enormous number of plane waves to properly represent densities within the unit cells of interesting chemical systems, the integrals are very simple to solve – this approach is used in solid-state physics.

Even in the cases where contracted GTOs are chosen as basis sets, DFT converge with respect to basis-set size more rapidly than MO techniques. Polarized valence double- ζ basis sets are quite adequate for a wide variety of calculations, and very good convergence in many properties can be seen with polarized triple- ζ basis sets (with diffuse functions as necessary). Besides issues associated with basis sets, considerable progress has been made in developing linear-scaling algorithms for DFT.

Note that SCF convergence in DFT is sometimes more problematic than in HF. KS and HF orbitals are similar – the convergence problem can often be very effectively alleviated by using the HF orbitals as an initial guess for the KS orbitals. HF orbitals can usually be generated quite quickly, therefore, the extra step can ultimately be time-saving if it is sufficiently improves the KS SCF convergence.

Systematic improvability

In MO theory, there is a clear and well-defined path to the exact solution of the Schrödinger equation – to express our wave function as a linear combination of all possible configurations (full CI) and choose a basis set that is infinite in size. While such a goal is essentially never practicable, at least the path to it can be followed unambiguously until computational resources fail.

With DFT, the situation is much less clear when we want to improve our calculations. As all current density functionals are approximate for arbitrary molecular systems, there is no obvious way to determine beforehand which functional may be optimal for a particular case of interest. Moreover, once the result is in hand, there is really no way to evaluate its accuracy. Just as with MO theory one can examine basis-set convergence, but that does not address how good or bad the functional is.

Nevertheless, for many interesting systems, some experimental data do exist, and it is thus possible to better benchmark whether a given DFT functional performs adequately against those data. In addition, experience dictates that, across a surprisingly wide variety of systems, DFT tends to be quite robust.

Worst-case scenarios

Certain failures of modern DFT should be anticipated or easily explained. One clear problem with modern functionals is that they make the energy a function entirely of the local density and possibly the density gradient – they are incapable of properly describing London dispersion forces, which derive entirely from electron correlation at ‘long range’. Adding HF exchange to the DFT functional cannot completely alleviate this problem – the HF level of theory does not account in any way for opposite-spin electron correlation. Example – noble gas dimers like He_2 , Ne_2 , etc., have potential energy minima at van der Waals contact, but DFT predicts the potential energy curve for these diatomics to be purely repulsive, at least as long as saturated basis sets are used. With incomplete basis sets, BSSE can introduce a spurious minimum at about the right position, but this is purely fortuitous – the physics of dispersion is simply not included in the functionals. This is an active research area.

Other problems with non-bonded complexes: in hydrogen-bonded systems, heavy-atom-heavy-atom distances tend to be sensitive to the functional used. These distances predicted by GGA DFT are typically too short by about 0.1 Å, but the interaction energies are often reasonably well predicted. A basis set including diffuse functions should be employed, otherwise large errors can be observed for intramolecular hydrogen bonds.

More problematic: charge-transfer intermolecular complexes.

Modern DFT functionals have a tendency to predict such interactions to be stronger than they should be. Example: some pure DFT functionals overestimated the binding of ethylene and molecular fluorine by 20 kcal/mol. Including HF exchange alleviates the problem to some extent, but only by cancellation of errors, since HF theory incorrectly predicts the interaction between ethylene and molecular fluorine to be purely repulsive.

General performance overview of DFT

The general picture for DFT is quite bright. For the ‘average’ problem, DFT is the method of choice to achieve a particular level of accuracy at lowest cost.

Energetics: Exact DFT is an ab initio theory (even if most modern implementations may be regarded as having semiempirical flavor). The quality with respect to energetic predictions is usually judged based on its performance for atomization energies. Table on the next page collects average mean and maximal (in parentheses) absolute error in kcal/mol for four test sets of molecules: A – G2 subset, 32 molecules containing only first-row atoms; B – G2 set, 55 molecules including first- and second-row atoms; C – 108 molecules including first- and second-row atoms; D – G2/97 set, 148 molecules including first- and second-row atoms. The G2/97 set includes substituted hydrocarbons, radicals, inorganic hydrides, unsaturated ring hydrocarbons, and polyhalogenated organics and inorganics.

Level of theory	Test sets			
	A	B	C	D
MO theoretical methods				
HF/6-31G(d)	85.9	80.5 (184.3)		
HF/6-31G(d,p)			119.2	
HF/6-311G(2df,p)	82.0			
HF/6-311+G(3df,2p)		74.5 (170.0)		
MP2/6-31G(d)	22.4	16.0 (40.3)		
MP2/6-31G(d,p)	23.7		22.0	
MP2/6-311+G(3df,2p)		7.3 (25.4)		
QCISD/6-31G(d)	28.8			
CCSD(T)/6-311G(2df,p)	11.5			
G2(MP2)				1.8 (8.8)
CBS-4				2.7 (12.9)
G2	1.2	1.2		1.4 (10.6)
CBS-q				2.3 (11.4)
CBS-Q				1.2 (8.1)
G3				0.9 (4.9)

Level of theory	Test sets			
	A	B	C	D
LSDA functionals				
SVWN/6-31G(d)	35.7	36.4 (84.0)		
SVWN/6-31G(d,p)			52.2	
SVWN/TZ2P			50.1	
SVWN/6-311+G(2df,p)	43.5			90.9 (228.7)
GGA functionals				
BWVN/6-31G(d)	4.4			
BLYP/6-31G(d)	5.6	5.3 (18.8)		
BLYP/6-31G(d,p)			7.0	
BLYP/6-31+G(d)		4.4 (16.3)		
BLYP/6-311G(2df,p)	9.6			
BLYP/6-311+G(3df,2p)		5.0 (15.8)		7.1 (28.4)
BLYP/6-311++G(3df,3pd)	9.6			
BP86/6-31G(d)		7.2 (24.0)		
BP86/6-311+G(3df,2p)		10.3 (25.4)		20.2 (49.7)
BPW91/6-31G(d,p)			7.4	
BPW91/6-311+G(3df,2p)				7.8 (32.2)

Level of theory	Test sets			
	A	B	C	D
BPW91/6-311++G(3df,3pd)	6.0			
EDF1/6-31+G(d)		3.2 (15.3)		
PBE/6-311+G(3df,2p)		8.6 (26.0)		
PWPW91/6-311++G(3df,3pd)	8.6			
<i>m</i> PWPW91/6-311++G(3df,3pd)	6.7			
VSXC/6-311+G(3df,2p)		2.5 (10.0)		
Hybrid functionals				
BH&HLYP/6-311++(3df,3pd)	11.7 (23.4)			
B1LYP/6-311++(3df,3pd)	3.1 (12.2)			
B1PW91/6-311++(3df,3pd)	5.4 (14.3)			
<i>m</i> PW1PW91/6-311++G(3df,3pd)	3.5 (6.7)			
PBE1PBE/6-311++G(3df,3pd)		3.5 (10.0)		
B3LYP/6-31G(d)		5.2 (31.5)	6.8	
B3LYP/6-31+G(d)		5.9 (35.9)		
B3LYP/6-311+G(3df,2p)		2.2 (8.4)		3.4 (24.1)
B3LYP/aug-cc-pVTZ		2.6 (18.2)		
B3LYP/6-311++(3df,3pd)		3.3		

Level of theory	Test sets			
	A	B	C	D
B3P86/6-31G(d)		5.9 (22.6)		
B3P86/6-311+G(3df,2p)		7.8 (22.7)		18.0 (49.2)
B3PW91/6-31G(d,p)			6.8	
B3PW91/6-311+G(3df,2p)				3.5 (21.8)
B3PW91/6-311++G(3df,3pd)	4.8			
<i>m</i> PW3PW91/6-311++G(3df,3pd)	2.7 (7.4)			

There are some key points inferred from this Table:

- 1) For a given average level of accuracy, hybrid DFT methods are the most efficient, with mean absolute errors almost equal in quality to the much more expensive multilevel correlated methods. However, the maximum absolute errors are much large – DFT functionals are less general and less reliable.
- 2) Hybrid DFT funmctionals are usually better than corresponding pure DFT functionals.
- 3) Increasing basis-set size does not always improve the accuracy of the DFT models, although it must ultimately lead to a converged prediction.
- 4) Of the currently available DFT models, GGA offer a major improvement over the older LSDA model. The P86 functional should be avoided. There is no clear preference amongst the remaining functionals, other than the hybrid functionals tend to outperform the pure functionals. B3LYP is slightly better than the others and historically it has become the most popular DFT method. The noteworthy exceptions are EDF1 and VSXC – it will be interesting to see more data calculated by these methods.

The utility of DFT in computing the bond strengths between transition metals and hydrides, methyl groups, and methylene groups has also been demonstrated. Because of the non-dynamical correlation problem associated with the partially filled metal d orbitals, such binding energies are usually very poorly predicted by MO methods until high levels are used for correlation.

Mean absolute errors in metal-ligand binding energies (kcal/mol)

Level of theory	H	CH ₃	CH ₂
MO: MCPF	6	9	20
QCISD(T)		6	
PCI-80	2	2	4
DFT: SVWN	12		
BP86	8		
BH&HLYP			16
BH&HLYP/ECP		5	9
B3LYP	5	6	4
B3LYP/ECP		9	7

In the area of reaction energetics, Andzelm et al. have compared levels of theory for the enthalpies of forward activation and reaction for organic reactions, the unimolecular rearrangements:

- 1) vinyl alcohol \rightarrow acetaldehyde;
- 2) cyclobutene \rightarrow *s-trans*-butadiene;
- 3) cyclopropyl radical \rightarrow allyl radical;

the unimolecular decompositions:

- 1) tetrazine \rightarrow 2HCN + N₂;
- 2) trifluoromethanol \rightarrow carbonyl difluoride + HF;

the bimolecular condensation reactions:

- 1) butadiene + ethylene \rightarrow cyclohexene (the Diels-Alder) reaction;
- 2) methyl radical + ethylene \rightarrow propyl radical;
- 3) methyl radical + formaldehyde \rightarrow ethoxyl radical;

and the bimolecular exchange reactions:

- 1) FO + H₂ \rightarrow FOH + H;
 - 2) HO + H₂ \rightarrow H₂O + H;
 - 3) H + acetylene \rightarrow H₂ + HC₂;
-

Here are the mean and maximal absolute errors (kcal/mol):

Level of theory	Activation		Reaction	
	Mean	Maximum	Mean	Maximum
MNDO	23.4	51.8	10.9	57.7
AM1	9.3	34.2	7.5	22.1
HF/6-31G(d)	13.6	30.6	10.5	24.8
MP2/6-31G(d)	9.9	28.8	6.3	26.0
BLYP/6-31G(d)	5.9	21.9	5.9	13.0
B3PW91/6-31G(d)	3.7	12.9	6.8	17.7

The pure DFT BLYP functional badly underestimates the activation enthalpies for H-atom transfer reactions. Many other authors noted this behavior – motivation for MPW1K.

St-Amant et al. (1995) have analyzed the utility of HF, MP2, LSDA, and BP86, using basis sets of DZP to TZP quality, for the prediction of 35 conformational energy differences in small to medium-size organic molecules and found the mean absolute errors for these four methods as 0.5, 0.4, 0.6, and 0.4 kcal/mol, respectively; the average conformational energy difference is 1.6 kcal/mol. A large amount of data exists evaluating the utility of DFT for computing ionization potentials and electron affinities using a Δ SCF approach. The conclusions are similar to those made for enthalpies of formation (atomization energies), except that there is much less, if any, preference for hybrid functionals over pure functionals, so long as P86 is avoided. Atomic and molecular proton affinities (PAs) has also been evaluated for various functionals for ammonia, water, acetylene, silane, phosphine, silylene, hydrochloric acid, and molecular hydrogen. For G2 and G3 theories, the mean absolute errors in PAs are 1.1 and 1.3 kcal/mol, respectively. At the SVWN, BLYP, BP86, BPW91, B3LYP, B3P86, and B3PW91 levels with the 6-311+G(3df,2p) basis set, the corresponding errors are 5.8, 1.8, 1.5, 1.5, 1.3, 1.1, and 1.2 kcal/mol, respectively. The much cheaper hybrid DFT methods are thus entirely competitive with G2 and G3.

Geometries

Analytic first derivatives are available for almost all density functionals – geometry optimization can be easily carried out. The performance of the various functionals is usually quite good for predicting minimum energy structures. Bond lengths at the LDA level for molecules composed of first- and second-row atoms are typically as good as those predicted by MP2; both these levels perform better than HF. GGA functionals does not usually improve LDA, but GGAs tend to overestimate bond lengths.

Mean absolute errors in bond lengths (Å) for different methods

Level of theory	Test sets		
	A	B	C
MO theoretical methods			
HF	0.022	0.021	
MP2	0.014	0.014	0.022
QCISD	0.013		
CCSD(T)	0.005		
LSDA functionals			
SVWN	0.017	0.016	
GGA functionals			
BLYP	0.014	0.021	0.048
BPW91	0.014	0.017	0.020

Level of theory	Test sets		
	A	B	C
PBE	0.012		
PWPW91	0.012		
<i>m</i> PWPW91	0.012		
Hybrid functionals			
BH&HLYP	0.015		
B1LYP	0.005		
B1PW91	0.010		
<i>m</i> PW1PW91	0.010		
PBE1PBE	0.012		
B3LYP	0.004		0.030
B3PW91	0.008	0.011	0.020
<i>m</i> PW3PW91	0.008		

The hybrid functionals, which mix GGA with HF (the HF level tends to systematically underestimate bond lengths), give noticeable improvement in predicted bond lengths. Very small improvements in geometrical accuracy are usually noted with increasing basis set size beyond polarized double- ζ quality.

Accuracies in bond angles for all flavors of DFT average about 1° , the same as is found for MP2. For dihedral angles, HF, MP2, and DFT all perform equivalently. The most popular functionals (B3LYP) are as accurate for molecules containing third-row main-group elements as they are for molecules of lighter elements. The LYP correlation functional in this case seems to be inferior as compared to PW91.

However, for the transition metals, DFT has proven to be a tremendous improvement over HF and post-HF methods, particularly for cases where the metal atom is coordinatively unsaturated. The narrow separation between filled and empty d orbitals typically leads to enormous non-dynamical correlation problems with an HF treatment, and DFT is much less prone to analogous problems. Even in cases of a saturated coordination sphere, DFT methods significantly outperform HF or MP2. Jonas and Thiel (1995) used the BP86 functional to compute geometries for the neutral hexacarbonyl complexes of Cr, Mo, and W, the pentacarbonyl complexes of Fe, Ru, and Os, and the tetracarbonyl complexes of Ni, Pd, and Pt. Over the 10 unique metal-carbon bond lengths for which experimental data are available, they observed no error in excess of 0.01 Å except for W (0.017 Å). At the HF and MP2 levels using equivalent basis sets, the corresponding average absolute errors are 0.086 and 0.028 Å, respectively, and the maximum deviations are 0.239 and 0.123 Å.

DFT shows systematic weaknesses in geometries in those areas where it similarly does poorly for energetics: van der Waals complexes tend to have interfragment distances that are too large because the dispersion-induced attraction is not properly modeled. Hydrogen bonds are somewhat too short as a rule, and most charge transfer complexes have their polarities overestimated so that they are too tightly bound.

Houk and coworkers (1997) have studied a large number of TS structures for organic electrocyclic reactions and concluded that the B3LYP functional is very good for predicting geometries in this area. However, some problems can be found in ionic examples of such reactions.

Charge distributions

Over 108 molecules in test set B, the mean absolute errors in predicted dipole moments were computed to be 0.23, 0.20, 0.23, 0.19, and 0.16 D at the HF, MP2, SVWN, BPW91, and B3PW91 levels of theory, respectively, using the 6-31G(d,p) basis set. These results were somewhat improved with more complete basis sets. When one compares HF, MP2, BLYP, and B3LYP for predicting dipole moments, one can see that in general the performances of MP2, the pure BLYP functional, and the hybrid B3LYP functional are about equal, although both DFT functionals do very slightly better than MP2 in several cases. HF theory shows its typical ~10-15% overestimation of dipole moments, and its historically well-known reversal of moment for CO.

Dipole moments (D) for eight small molecules at four levels of theory using the very large POL basis set

Molecule	HF	MP2	BLYP	B3LYP	Experiment
NH ₃	1.62	1.52	1.48	1.52	1.47
H ₂ O	1.98	1.85	1.80	1.86	1.85
HF	1.92	1.80	1.75	1.80	1.83
PH ₃	0.71	0.62	0.59	0.62	0.57
H ₂ S	1.11	1.03	0.97	1.01	0.97
HCl	1.21	1.14	1.08	1.12	1.11
CO	-0.25	0.31	0.19	0.10	0.11
SO ₂	1.99	1.54	1.57	1.67	1.63