

1. The electron density as fundamental quantity

We have now built up a complete framework for molecular electronic structure, starting with the Hartree-Fock self-consistent field (HF-SCF) model and then adding in various levels of treatment of electron correlation (CI, MPn, CC, ...). But, the hierarchy is computationally expensive, does not lend itself well to things that are not molecular (like semi-conductors and metals), and is perhaps more complicated than it needs to be for many uses.

Recall for a system with n electrons, we've endeavored to solve the n electron Schrödinger equation:

$$\left\{ \sum_{i=1}^n \hat{h}_i + \sum_{i=1}^n \sum_{j=i+1}^n \frac{1}{|\mathbf{r}_j - \mathbf{r}_i|} \right\} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_n) = E \Psi(\mathbf{r}_1, \dots, \mathbf{r}_n)$$

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i}$$

But we *know* that electrons are *indistinguishable*, so somehow the wavefunction Ψ contains more information than we need or can even use. In fact, the only thing we directly observe is the *electron density*

$$\rho(\mathbf{r}) = \int \dots \int |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_n$$

$\rho(\mathbf{r})d\mathbf{r}$ gives the total number of electrons within some volume element, and has the property

$$n = \int \rho(\mathbf{r}) d\mathbf{r}$$

Can a theory be built just on this function? Yes!

2. Thomas-Fermi-Dirac model

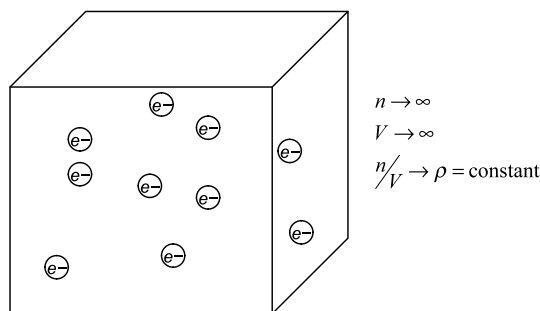
Thomas (1926) and Fermi (1928) independently hit on the idea of trying to construct a model for the atom based on its charge density ρ . Follow approach similar to Hartree and Fock: write down an expression for the energy in terms of kinetic and potential energy contributions, and appeal to variational principle to develop differential equation for ρ .

Nucleus-electron attraction...easy: $v[\rho(\mathbf{r})] = -Z \int \frac{\rho(\mathbf{r})}{r} d\mathbf{r}$

Electron-electron repulsion. Use classical repulsion, which *includes* self-interaction:

$$J[\rho(\mathbf{r})] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

Kinetic energy...hmmm. Here they get creative. Consider a *homogeneous electron gas*:



Using Fermi-Dirac statistics, able to show: $T_{\text{heg}}[\rho(\mathbf{r})] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}$

Notice each of these contribution is a function of a *function*, i.e., a “functional.” Hence the name *density functional theory*.

Now write total energy and apply variational principle:

$$E_{\text{TF}}[\rho(\mathbf{r})] = T_{\text{heg}} + v + J \quad \delta \left\{ E_{\text{TF}} - \lambda \left[\int \rho(\mathbf{r}) d\mathbf{r} - n \right] \right\} = 0$$

$$\lambda = \frac{\delta E_{\text{TF}}}{\delta \rho(\mathbf{r})} = \frac{1}{2} (3\pi^2)^{2/3} \rho^{2/3}(\mathbf{r}) - \frac{Z}{r} + \int \frac{\rho(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1$$

Solve last under constraint that total number of electrons is n , gives expression for ρ and by back-substitution for E . Notice appearance of *functional derivative*, similar in concept to a regular derivative, but involving variations with respect to the value of a function. We'll repeatedly see here, for instance, that

$$\frac{\delta J[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = \int \frac{\rho(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1 = v_{\text{Coulomb}}(\mathbf{r}) \quad \text{units of energy/charge}$$

Thomas-Fermi model is a conceptual triumph but a practical disaster, for instance molecules are not stable within this model. Dirac tried to fix up by including exchange, but still not a satisfactory model.

Several problems:

Homogeneous gas model for kinetic energy is a big error

Classical treatment of electron interactions (no exchange or correlation, and includes electron “self-interaction.”

3. Hartree-Fock-Slater model

Recall we've already seen another attempt to build a model that includes the density, HFS, developed by Slater in 1951. He took a different approach. Rather than trying to write everything in terms of density, though, he started with the Hartree-Fock equation:

$$\left\{ -\frac{\hbar^2}{2m_e} \nabla^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}} + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 - \sum_{j=1}^{N/2} \hat{K}_j \right\} \psi_i(\mathbf{r}_1) = \hat{f} \psi_i(\mathbf{r}_1) = \varepsilon_i \psi_i(\mathbf{r}_1)$$

$$\hat{K}_j \psi_i(\mathbf{r}_1) = \left[\int \psi_i(\mathbf{r}_2) \psi_j(\mathbf{r}_2) \frac{1}{r_{12}} d\mathbf{r}_2 \right] \psi_j(\mathbf{r}_1)$$

Restricted Hartree-Fock (RHF) equation

The Coulomb potential already is a functional of the density. The exchange potential $\sum_{j=1}^{N/2} \hat{K}_j$ is decidedly not, but by rewriting in terms of an exchange charge density

$$\sum_j \hat{K}_j \psi_i(\mathbf{r}_1) = \left[\int \frac{\rho_i^x(\mathbf{r}_1; \mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \right] \psi_i(\mathbf{r}_1), \quad \rho_i^x(\mathbf{r}_1; \mathbf{r}_2) = \sum_j \frac{\psi_i(\mathbf{r}_1) \psi_j(\mathbf{r}_2) \psi_j(\mathbf{r}_1) \psi_i(\mathbf{r}_2)}{\psi_i(\mathbf{r}_1) \psi_i(\mathbf{r}_2)}$$

he saw a way to approximate the exchange potential in terms of the density, drawing on homogeneous gas model:

$$v_{X,HFS}(\mathbf{r}_1) = -\frac{3}{2} \left[\frac{3\rho(\mathbf{r}_1)}{\pi} \right]^{1/3}$$

Can now write an approximate Hartree-Fock-Slater DFT equation:

$$\left\{ -\frac{\hbar^2}{2m_e} \nabla^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}} + \left[\int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \right] - \frac{3}{2} \alpha \left[\frac{3\rho(\mathbf{r}_1)}{\pi} \right]^{1/3} \right\} \psi_i(\mathbf{r}_1) = \hat{f}_{HFS} \psi_i(\mathbf{r}_1) = \epsilon_i \psi_i(\mathbf{r}_1)$$

This approximate model has is a hybrid, retaining wavefunctions but writing the potentials in terms of the density. Much simpler than Hartree-Fock and better than Thomas-Fermi, and anticipated modern DFT.

4. Hohenberg-Kohn theorems

This is all well and fine, but not rigorously grounded theoretically.

In 1964, Hohenberg and Walter Kohn (future Nobel Prize dude) proved two important theorems that put Slater's and similar work by Fermi and Dirac on firmer foundation.

First Hohenberg-Kohn theorem:

Consider a system of electrons moving in an external field $v(\mathbf{r})$ [e.g., like the field generated by a set of nuclei, $v(\mathbf{r}_1) = -\sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}}$]. "... $v(\mathbf{r})$ is (to within a constant) a unique functional of $\rho(\mathbf{r})$; since, in turn, $v(\mathbf{r})$ fixes \hat{H} we see that the full many-particle ground state $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n)$ is a unique functional of $\rho(\mathbf{r})$."

What does *that* mean? Basically, that there is a unique one-to-one mapping between $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n)$ and $\rho(\mathbf{r})$; knowing either one is just as good as knowing the other. In particular, the electron kinetic energy, potential energy, and total energy are all determined by knowing $\rho(\mathbf{r})$. Proof by *reductio ad absurdum*.

$$E_v[\rho] = T[\rho] + V_{ee}[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}$$

where the kinetic energy T and electron-electron repulsion V_{ee} are *universal* functionals of ρ .

Vindicates general approach of Thomas, Fermi, Dirac, and Slater: problem *can* be cast just in terms of densities!

Second Hohenberg-Kohn theorem:

" $E_v[\rho]$ assumes its minimal value for the correct [ground state] $\rho(\mathbf{r})$, if the admissible functions are restricted by the condition $n = \int \rho(\mathbf{r}) d\mathbf{r}$."

This is a statement of the *variational principle* for the density; the *right* ground-state density is the one that minimizes the total energy. Can be extended somewhat to excited states and degenerate states, but the exact formalism is not well developed.

Nice results, but T and V are unknown, so operationally, of what use is this?

5. Kohn-Sham construction

Problem with Hohenberg-Kohn theorems is that we've completely lost the big things that we thought we knew: the kinetic energy and the classical Coulomb repulsion. Kohn and Sham later showed how to recover them, and to cast the DFT equations into a solvable form.

What if the electrons were attracted to the nuclei but didn't interact with each other? Suppose too they moved in some potential \tilde{v} that gave them the same density as the real system. Then the problem would be simple, since we know that the non-interacting system is exactly solved by a Slater determinant of orthogonal orbitals:

$$\begin{aligned}\tilde{E}_v[\rho] &= \tilde{T}[\rho] + \int \rho(\mathbf{r})\tilde{v}(\mathbf{r})d\mathbf{r} \\ \tilde{\Psi} &= |\tilde{\psi}_1(\mathbf{r}_1) \cdots \tilde{\psi}_n(\mathbf{r}_n)|, \quad \rho(\mathbf{r}) = 2 \sum_i |\tilde{\psi}_i(\mathbf{r})|^2 \\ \tilde{T}[\rho] &= \left\langle \tilde{\Psi} \left| -\frac{1}{2} \sum_i \nabla_i^2 \right| \tilde{\Psi} \right\rangle\end{aligned}$$

Variational principle then gives

$$\left[-\frac{1}{2} \nabla^2 + \tilde{v}(\mathbf{r}) \right] \tilde{\psi}_i = \epsilon_i \tilde{\psi}_i$$

And so? We can construct \tilde{v} ! Define

$$E_{xc}[\rho] = T[\rho] - \tilde{T}[\rho] + V_{ee}[\rho] - J[\rho]$$

Then

$$\begin{aligned}E_v[\rho] &= \tilde{T}[\rho] + J[\rho] + E_{xc}[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \\ \tilde{v}[\rho] &= \frac{\delta J}{\delta \rho} + \frac{\delta E_{xc}}{\delta \rho} + v(\mathbf{r}) = v_{Coulomb}(\mathbf{r}) + v_{xc}[\rho] + v(\mathbf{r})\end{aligned}$$

Kohn-Sham equation

$$\left[-\frac{1}{2} \nabla^2 + v(\mathbf{r}) + v_{Coulomb}(\mathbf{r}) + v_{xc}[\rho] \right] \tilde{\psi}_i = \epsilon_i \tilde{\psi}_i$$

This is an *exact* one-electron equation for the real, fully interacting system. It includes the *exchange-correlation functional*, $v_{xc}[\rho]$, which is the difference between the classical electron-electron repulsion and the real interaction plus the difference in kinetic energies of the non-interacting and real systems. K-S formally swept everything that is hard to figure out into v_{xc} !

If we recall that $\hat{h} = -\frac{1}{2} \nabla^2 + v(\mathbf{r})$, then we see that

Hartree-Fock-Slater is a K-S theory with $v_{xc}[\rho] = -\frac{3}{2} \alpha \left[\frac{3\rho(\mathbf{r}_1)}{\pi} \right]^{1/3}$, a *local* functional of ρ

Hartree-Fock is a K-S theory with $v_{xc}[\rho] = -\sum_j \hat{K}_j$, a decidedly *non-local* functional of ρ

The KS orbitals are strictly not identical to one-electron wavefunctions, since they are just a fiction to describe the density. Koopman's theorem does not apply to them. In practice, though, they behave a lot like Hartree-Fock orbitals (sometimes better!), and tricks can be used to extract excitation and ionization energies.

6. Exchange-correlation functionals

So Kohn et al. showed that the DFT approach is theoretically well-grounded and provided one way to practically apply it. Promise is that if we can find an approximation to the (unknown) true v_{xc} with the right balance of simplicity and accuracy, we will have one sweet theory. Has to incorporate both *exchange*, like Slater tried to do, and *correlation*.

How to proceed? Lots of approaches, and jargon here is at least as bad as in wavefunction-based methods. Perdew 2006 describes the “Jacob’s ladder” of approximations:

Local (spin) density approximation [L(S)DA]

One well-defined limit is the homogeneous electron gas, and this is the usual starting point for modern approximate DFT methods. Assume exchange and correlation potentials at any given point depend only on the value of ρ there (or spin-up and spin-down ρ , if spin-polarized). We know from Slater and Dirac’s work what the exchange potential is for this system.

It is possible to determine numerically the correlation energy for a given density from quantum Monte Carlo calculations. Ceperley and Alder (*PRL* **1980**, *45*, 566) did this to very high accuracy, and others (Vosko, Wilk, and Nusair, “VWN”, and Perdew and Wang, “PW”) fit these numerical results to analytical models in ρ . This combination of local exchange and correlation defines the LDA model.

LDA offers modest improvement over HFS for molecules. “Homogeneous” approximation pretty severe for an atom or molecule. Nonetheless, works surprisingly well for structures and charge distributions, but has problems in calculating accurate bond energies, typically overbinding. Also tends to underestimate the HOMO-LUMO gap in molecules and analogous band gap in solids.

Generalized gradient approximation [GGA]

In the spirit of a Taylor expansion of $v_{xc}[\rho]$, next logical elaboration to add is the (“semi-local”) dimensionless reduced *gradient* of the density:

$$v_{\text{GGA}} = v_{\text{xc}} \left[\rho, \frac{|\nabla \rho(\mathbf{r})|}{\rho^{4/3}(\mathbf{r})} \right].$$

This gradient can be calculated relatively easily, but how to include in a functional?

Two general philosophies, one *semi-empirical*, that is, fit to reproduce some known experimental data, and the other *non-empirical*, or designed to satisfy some set of well-established analytical constraints, like the size of the exchange hole or the analogous (but smaller) correlation hole. Generally constructed as add-ons to the LSDA, with separate treatments of exchange and correlation parts. Functional forms are complicated.

Most venerable semi-empirical one is “BLYP,” including Becke exchange functional and “Lee-Yang-Parr” correlation functional, developed in 1980’s. Of the non-empirical type, the “PW91” (Perdew-Wang 1991) and the “PBE” (Perdew-Becke-Ernzenhof). revPBE and RPBE are empirical corrections to PBE that attempt to improve bond energy predictions.

The GGA typically makes bond lengths a little short, but it does much better than LSDA for calculating bond energies. Overall a very good balance of performance and speed, especially for inorganic and bulk systems. A modern workhorse.

Meta-GGA

If first derivatives of ρ are good, then second-derivatives are better? Methods have been developed including the Laplacian of ρ , $\nabla^2 \rho$. These can have problems with numerical stability and the improvements in properties are not clear. Another quantity that does help is the *kinetic energy density*, which includes the gradient norms of the occupied orbitals:

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla \tilde{\psi}_i(\mathbf{r})|^2$$

This term also appears in the Taylor expansion of the exchange hole. Functionals that use this are *tau* functionals. The TPSS functional (Tao, Perdew, Staroverov, and Scuseria) is perhaps most prominent. Many other meta-GGAs, but none have gained wide acceptance. Typically improvements in performance appear not to compensate for the additional computational cost, but this is still under development.

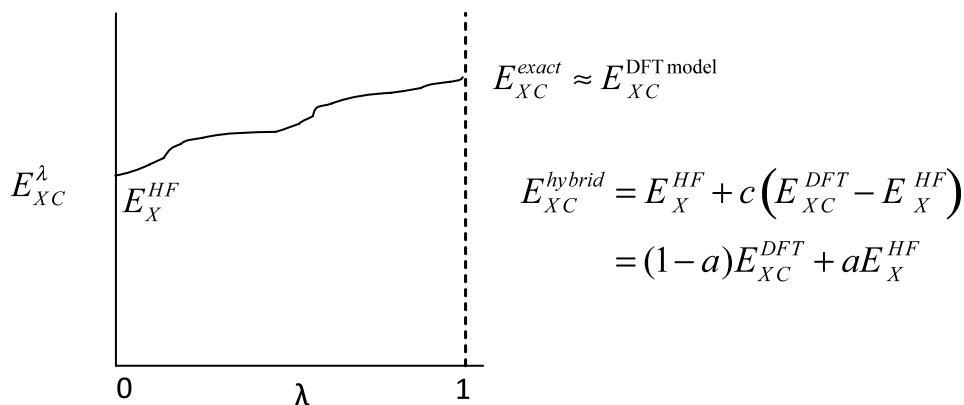
Hyper-GGA and hybrid functionals

Next step in improvements is to reintroduce exact exchange for the occupied orbitals. Based on *adiabatic connection*. Can show

$$E_{XC}[\rho] = \int v_{XC}[\rho] \rho d\mathbf{r} = \int_0^1 \left[\int v_{XC}^\lambda[\rho] \rho d\mathbf{r} \right] d\lambda$$

where λ scales the electron-electron repulsion according to $\frac{\lambda}{|\mathbf{r}_1 - \mathbf{r}_2|}$. $\lambda = 0$ corresponds to the non-interacting system, described exactly by the Slater determinant of K-S orbitals. There is no correlation energy in this limit, and the exchange energy is exactly just the H-F exchange. $\lambda > 0$ we do not know, but at $\lambda = 1$ we have the “fully interacting” system, which is what we have been trying to describe with LDA and GGA and

Idea of a “hybrid” functional is to approximate the integral as a sum:



Up side is that we exactly capture some portion of the “exact” exchange. Downside is that now, in SCF procedure, have to calculate expensive HF exchange *plus* DFT functionals. And, what are we going to choose for the particular DFT model? LSDA? GGA? And, what are the integration constants going to be? In fact, it is found that the “right” amount of mixing depends on the molecule! Obviously huge amount of room for empiricism here.

Nonetheless, exact exchange does generally improve performance for things like bond energies, if for no other reason because errors in HF and GGA tend to go in opposite directions, so mixing them might seem to help.

Most venerable hybrid functional is “B3LYP,” which adds in H-F exchange to BLYP functional. End up in total with 8 (!) parameters amongst the DFT functionals and H-F mixing, fitted to various pieces of electronic structure and thermodynamic data. Often said to be roughly equivalent in performance to MP2, although much cheaper calculation.

PBE0 another hybrid generated from the less-empirical PBE GGA:

$$E_{xc}^{\text{hyb}}(n=4) = E_{xc}^{\text{DFA}} + \frac{1}{4} (E_x - E_x^{\text{DFA}}). \quad (11)$$

, Perdew et al., *JCP* **1996**, *105*, 9982

Following from Paier et al., *JCP* **2005**, *122*, 234102:

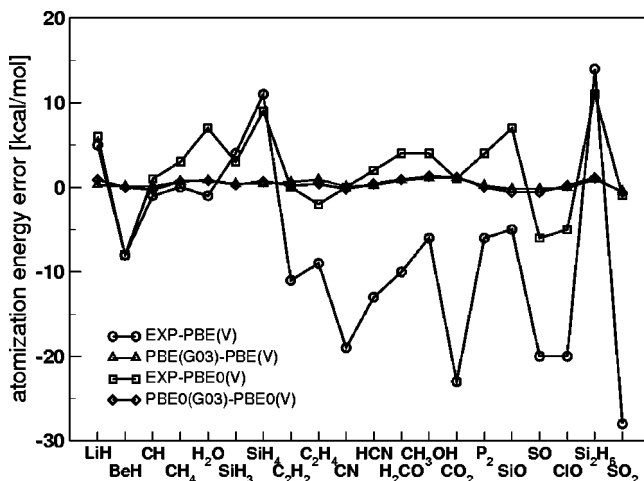


FIG. 1. Atomization energy errors for selected molecules given in Tables II and III for the PBE and PBE0 functionals, respectively. The setup of the calculations is described in Sec. III. Deviations from experiment and G03 calculations are shown as well. The theoretical values of the atomization energies were calculated without ZPE correction.

There are many, *many* other hybrid functionals. Truhlar has a small industry in developing hybrid functionals of various sorts fitted to various data. People like them, because you can fit them to your favorite dataset. Not necessarily so satisfying theoretically, but good results can be got.

Perhaps there is some theoretically “right” way to incorporate exact exchange in a “hyper-GGA”, but it remains to be elucidated.

Beyond hyper-GGA

Beyond exact exchange lies the exact answer. The path to that point is not clear, and this is one of the big weaknesses of DFT vs. wavefunction methods, is that there is not clear cut, systematic way to improve the theory.

Worth mentioning the emerging class of “double hybrid” functionals, in which both some amount of HF exchange and MP2 correlation are added into the potential. Stay tuned.

Cramer Table 8.7 has a nice summary of many popular functionals.

7. Implementations

Implementations largely follow that of what we described before for Hartree-Fock and the Hartree-Fock-Roothaan equations. Expand in a basis, make an initial guess at the coefficients/density, construct and diagonalize matrix, get new coefficients and iterate.

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i} \quad \text{or} \quad \mathbf{FC} = \mathbf{SC}\epsilon$$

$$F_{\mu\nu} = \langle \phi_\mu | \hat{f} | \phi_\nu \rangle \quad S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$$

$$F_{\mu\nu} = \langle \phi_\mu | \hat{h} | \phi_\nu \rangle + \langle \phi_\mu | v_{Coulomb}[\rho] | \phi_\nu \rangle - \langle \phi_\mu | v_{XC}[\rho] | \phi_\nu \rangle$$

Big impediment was development of effective numerical quadrature for evaluating matrix elements over complicated XC functionals, especially when energy gradients are involved. Problem akin to Pulay forces that appear in incomplete basis. Now seems to be a licked problem. First and second derivative of total energy are implemented in many codes, so methods can be used like H-F. Same caveats about initial guesses, convergence criteria and algorithms, be sure to use the *same computational parameters* when comparing results on different molecules, etc.

Gaussian allows separate specification of exchange and correlation functional and wide latitude on how they are mixed and matched.

DFT appears to be less basis-set dependent than H-F and beyond. Pople basis sets particularly popular. Since equations must be solved numerically, though, no reason necessarily to prefer a Gaussian basis, and efficient pure-DFT codes built around STO's (ADF), numerical basis functions (DMol), and as we will see, plane-waves. Exact solutions within the model calculations are possible using specialized approaches.

Very common approach for improving computational efficiency is to expand density in a secondary, density-fitting basis set. Implemented in ADF, available in Gaussian and some other similar codes.

8. Performance

Very active area of research. Cramer, section 8.6, has a nice tabulation of comparisons of results for many systems.

DFT functionals of today fail in cases where exchange and correlation are really important, like dissociating molecules or highly correlated electronic systems or vdW interactions. Performance for activation energies less satisfactory than for ground states. Specialized parameterizations and even functionals have been devised for these specific problems. On other hand, DFT does much better than H-F and MP2 for properties of inorganic systems.

GGA functionals improve over LSDA in terms of energetics. The improvement from GGA to Meta-GGA is not as large as that from LSDA to GGA. For accurate energies some exact exchange is needed, although systematically improved functionals such as TPSS do outperform hybrids.

Open-shell DFT calculations are less prone to spin contamination than is HF.

Back to our difluoroethane example:

	HF/3-21G		G2		PBE/6-31G(d)		B3LYP/6-31G(d)	
	F-C-C-F angle (deg)	E_{rel} (kJ/mol)	F-C-C-F angle (deg)	E_{rel} (kJ/mol)	F-C-C-F angle (deg)	E_{rel} (kJ/mol)	F-C-C-F angle (deg)	E_{rel} (kJ/mol)
<i>trans</i>	180.0	0	180.0	0	180.0	0	180.0	0
<i>gauche</i>	74.97	3.5	68.94	3.3	69.80	2.9	69.89	1.6
TS	121.3	11.99			124.2	11.31	123.55	11.87
eclipsed	0	38	0	26.7	0.0	28.1	0.0	29.3

9. Resources:

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R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University, New York, 1989.

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