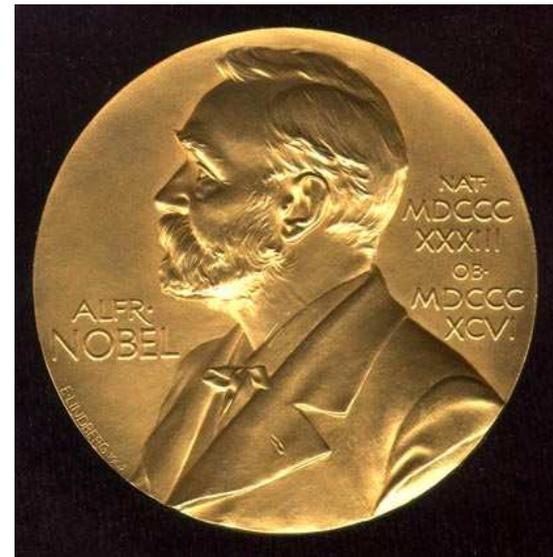


Walter Kohn was awarded with the Nobel Prize in Chemistry in 1998 for his development of the density functional theory.



Walter Kohn receiving his Nobel Prize from His Majesty the King at the Stockholm Concert Hall.

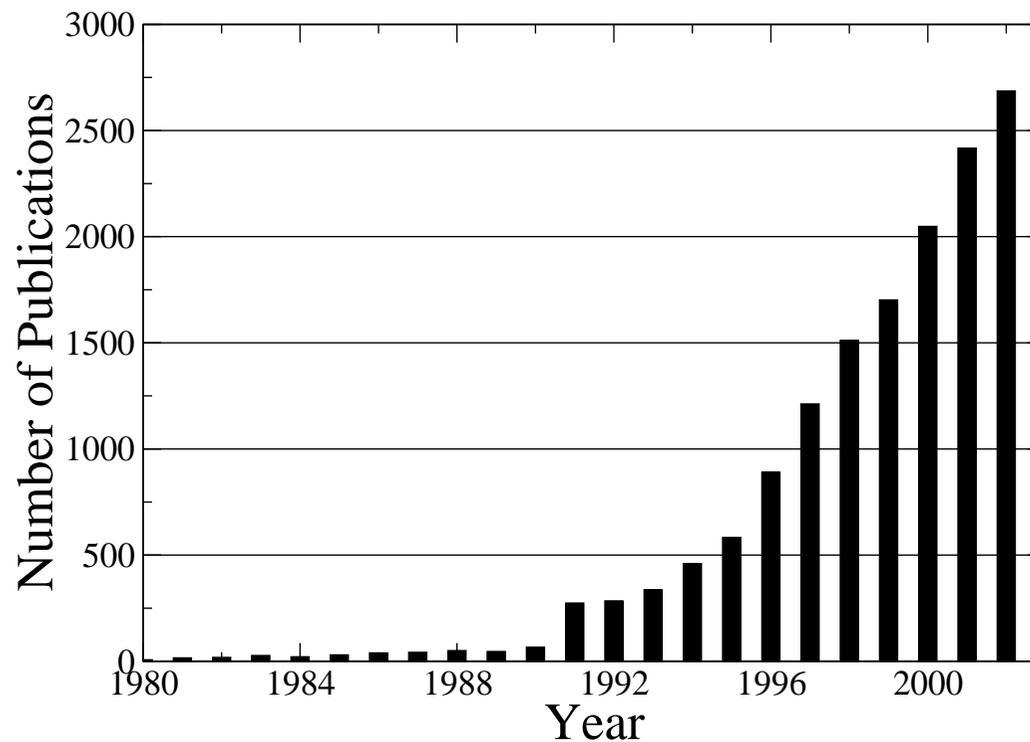


The Nobel Prize medal.

The Density Functional Theory was introduced in two seminal papers in the 60's:

1. Hohenberg-Kohn (1964): ~ 4000 citations
2. Kohn-Sham (1965): ~ 9000 citations

The following figure shows the number of publications where the phrase “density functional theory” appears in the title or abstract (taken from the ISI Web of Science).



Density functional theory (DFT) is an approach to the electronic structure of atoms and molecules which has enjoyed a dramatic surge of interest since the late 1980s and 1990s [Parr 1983; Wimmer 1997]. Our approach here will be to introduce the key elements of the theory and to identify the similarities and differences between DFT and the Hartree-Fock approach. In Hartree-Fock theory the multi-electron wavefunction is expressed as a Slater determinant which is constructed from a set of N single-electron wavefunctions (N being the number of electrons in the molecule). DFT also considers single-electron functions. However, whereas Hartree-Fock theory does indeed calculate the full N -electron wavefunction, density functional theory only attempts to calculate the total electronic energy and the overall electronic density distribution. The central idea underpinning DFT is that there is a relationship between the total electronic energy and the overall electronic density. This is not a particularly new idea; indeed an approximate model developed in the late 1920s (the Thomas-Fermi model) contains some of the basic elements. However, the real breakthrough came with a paper by Hohenberg and Kohn in 1964 [Hohenberg and Kohn 1964], who showed that the ground-state energy and other properties of a system were uniquely defined by the electron density. This is sometimes expressed by stating that the energy, E , is a unique *functional* of $\rho(\mathbf{r})$.

The second landmark paper in the development of density functional theory was by Kohn* and Sham who suggested a practical way to solve the Hohnberg–Kohn theorem for a set of interacting electrons [Kohn and Sham 1965]. The difficulty with Equation (3.37) is that we do not know what the function $F[\rho(\mathbf{r})]$ is. Kohn and Sham suggested that $F[\rho(\mathbf{r})]$ should be approximated as the sum of three terms:

$$F[\rho(\mathbf{r})] = E_{\text{KE}}[\rho(\mathbf{r})] + E_{\text{H}}[\rho(\mathbf{r})] + E_{\text{XC}}[\rho(\mathbf{r})] \quad (3.42)$$

where $E_{\text{KE}}[\rho(\mathbf{r})]$ is the kinetic energy, $E_{\text{H}}[\rho(\mathbf{r})]$ is the electron–electron Coulombic energy, and $E_{\text{XC}}[\rho(\mathbf{r})]$ contains contributions from exchange and correlation. It is important to note that the first term in Equation (3.42), $E_{\text{KE}}[\rho(\mathbf{r})]$, is defined as the kinetic energy of a system of *non-interacting* electrons with the same density $\rho(\mathbf{r})$ as the real system:

$$E_{\text{KE}}[\rho(\mathbf{r})] = \sum_{i=1}^N \int \psi_i(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \psi_i(\mathbf{r}) d\mathbf{r} \quad (3.43)$$

The second term, $E_{\text{H}}(\rho)$, is also known as the Hartree electrostatic energy. The Hartree approach to solving the Schrödinger equation was introduced briefly in Section 2.3.3 and almost immediately dismissed because it fails to recognise that electronic motions are correlated. In the Hartree approach this electrostatic energy arises from the classical interaction between two charge densities, which, when summed over all possible pairwise interactions, gives:

$$E_{\text{H}}[\rho(\mathbf{r})] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (3.44)$$

Combining these two and adding the electron–nuclear interaction leads to the full expression for the energy of an N -electron system within the Kohn–Sham scheme:

$$\begin{aligned}
 E[\rho(\mathbf{r})] = & \sum_{i=1}^N \int \psi_i(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \psi_i(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{XC}}[\rho(\mathbf{r})] \\
 & - \sum_{A=1}^M \int \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \rho(\mathbf{r}) d\mathbf{r}
 \end{aligned} \tag{3.45}$$

This equation acts to *define* the exchange–correlation energy functional $E_{\text{XC}}[\rho(\mathbf{r})]$, which thus contains not only contributions due to exchange and correlation but also a contribution due to the difference between the true kinetic energy of the system and $E_{\text{KE}}[\rho(\mathbf{r})]$.

Kohn and Sham wrote the density $\rho(\mathbf{r})$ of the system as the sum of the square moduli of a set of one-electron orthonormal orbitals:

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2 \tag{3.46}$$

By introducing this expression for the electron density and applying the appropriate variational condition the following one-electron Kohn-Sham equations result:

$$\left\{ -\frac{\nabla_1^2}{2} - \left(\sum_{A=1}^M \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + V_{\text{XC}}[\mathbf{r}_1] \right\} \psi_i(\mathbf{r}_1) = \varepsilon_i \psi_i(\mathbf{r}_1) \quad (3.47)$$

In Equation (3.47) we have written the external potential in the form appropriate to the interaction with M nuclei. ε_i are the orbital energies and V_{XC} is known as the exchange-correlation functional, related to the exchange-correlation energy by:

$$V_{\text{XC}}[\mathbf{r}] = \left(\frac{\delta E_{\text{XC}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \right) \quad (3.48)$$

The total electronic energy is then calculated from Equation (3.45).

To solve the Kohn-Sham equations a self-consistent approach is taken. An initial guess of the density is fed into Equation (3.47) from which a set of orbitals can be derived, leading to an improved value for the density, which is then used in the second iteration, and so on until convergence is achieved.

Why Density Functional Theory?

- Wavefunction based methods in QC to get correlation energy are quite time-consuming
 - MP2 scales N^5 , CCSD scales N^6
- DFT techniques provide a means for recovering correlation energy at a fraction of the computational cost
 - Can be made to scale linearly with the size of the molecular system.
 - Can be applied to 100s to 1000s of atoms
 - Can be formulated similarly to the standard SCF procedure
- By far, DFT is the most popular QC method used today.

What is DFT?

- Theoretical framework for utilizing the electron density as the primary variable to determining the properties of a molecular system.
- The Hohenberg-Kohn Theorem
 - There is a 1-to-1 mapping between the electron density and the exact ground state wavefunction
- Electron Density
 - The measure of the probability of finding an electron at a point in space.
 - A three-dimensional, physical observable

$$\Gamma = \int_{-\infty}^{\infty} \Psi^2 d\mathbf{r}$$

What is DFT?

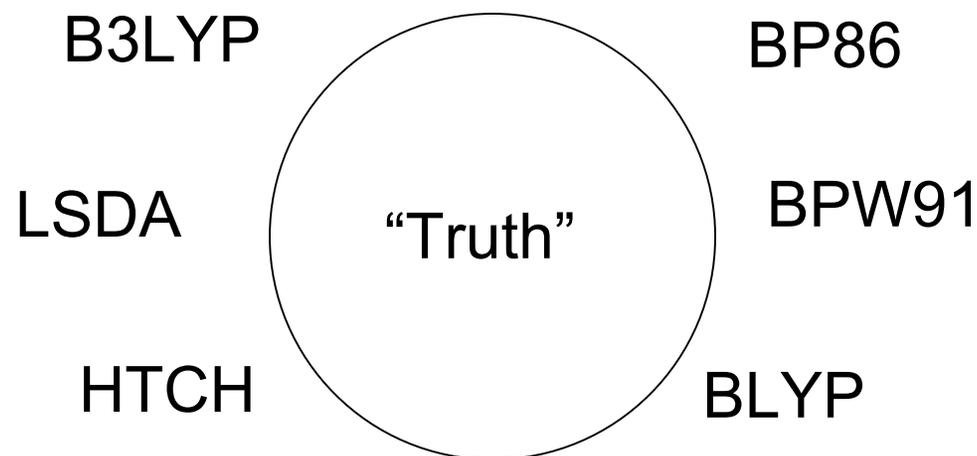
- In DFT, the energy of a molecular system is derived as a functional of the electron density

$$E[\rho] = T[\rho] + J[\rho] + V_N[\rho] + V_{xc}[\rho]$$

- If one knows the exact form of each of these terms, the energy and properties of a system by just plugging in the density
 - No basis sets, no determinants, no complicated computational procedures...

Here is the catch

- No one knows the exact form of the exact kinetic energy or the exchange-correlation functional
- No real systematic means for finding “truth”.
- Non-convergent QC



Kohn-Sham DFT

- Replace the exact kinetic energy with that of the kinetic energy of a non-interacting many electron system.

$$E[\rho] = T[\rho] + J[\rho] + V_N[\rho] + E_{xc}[\rho]$$

$$E[\rho] = T_s[\rho] + J[\rho] + V_N[\rho] + ((T[\rho] - T_s[\rho]) + E_{xc}[\rho])$$

- Many-electron interacting system -> Non-interacting reference system
- Mapped through an effective potential - adiabatic connection
- The wavefunction for the reference system is a Slater determinant!
 - Same functional form as HF theory, can use the same iterative SCF procedure to attack the problem.

KS-DFT in a finite basis

- E_{xc} is found as an integral over the a functional of variables of the density

$$E_{XC} = \int f(\rho_\alpha, \rho_\beta, \gamma_{\alpha\alpha}, \gamma_{\beta\beta}, \gamma_{\alpha\beta}) d\mathbf{r}$$

$$\gamma_{\alpha\alpha} = |\nabla\rho_\alpha|^2, \text{ gamma}_{\alpha\beta} = \nabla\rho_\alpha \cdot \nabla\rho_\beta$$

- The electron density in a finite basis can be expressed

$$\rho_\alpha(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu}^\alpha \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r}) \quad \nabla\rho_\alpha(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu}^\alpha \nabla(\phi_\nu(\mathbf{r})\phi_\mu(\mathbf{r}))$$

- Contributions to the Fock Matrix elements can be expressed as

$$Fxc_{\mu\nu}^\alpha = \int \left[\frac{\delta f}{\delta \rho_\alpha} \phi_\mu \phi_\nu + \left(2 \frac{\delta f}{\delta \gamma_{\alpha\alpha}} \right) * \nabla\rho_\alpha + \frac{\delta f}{\delta \gamma_{\alpha\beta}} \right] * \nabla\rho_\beta \cdot \nabla(\phi_\mu \phi_\nu) d\mathbf{r}$$

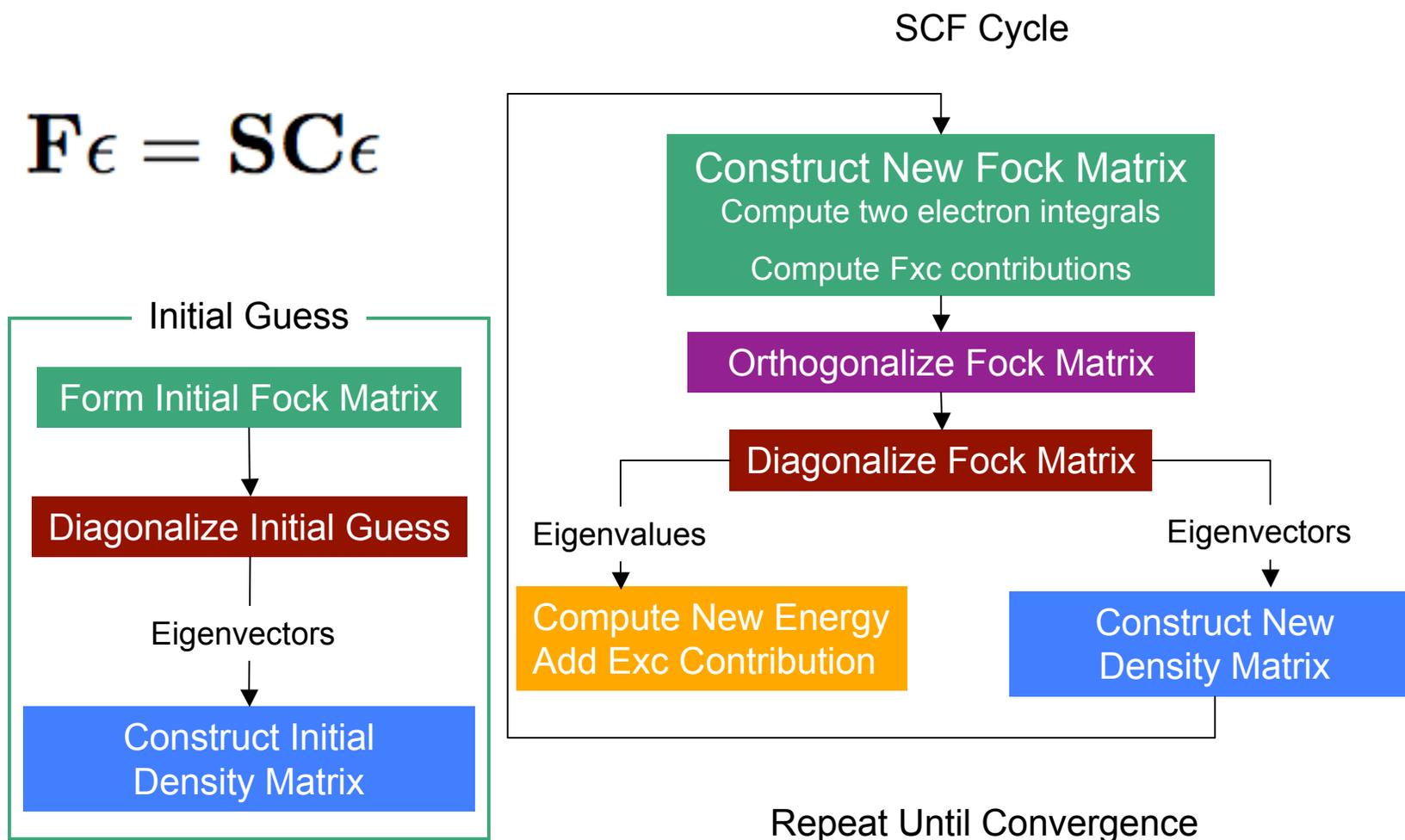
Interpreting KS-DFT

- As a consequence of obtaining a solution through SCF, we get KS orbitals
 - Not the same as HF orbitals
- Qualitatively, the shape of the orbitals are useful for analysis
- Application of this wavefunction for computing properties provides good results.

$$|\Psi_0\rangle = |\phi_1\phi_2 \dots \phi_N\rangle = (N!)^{-1/2} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \dots & \phi_N(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \dots & \phi_N(\mathbf{x}_2) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_1(\mathbf{x}_N) & \phi_2(\mathbf{x}_N) & \dots & \phi_N(\mathbf{x}_N) \end{vmatrix}$$

Modified KS DFT Self-Consistent Field Procedure

- The orbital coefficients that we are varying to minimize the energy are dependent on the energy, so an iterative procedure is used.



HF vs DFT

Key difference

- DFT as derived so far contains no approximations: it is exact.
- But, we need to know E_{xc} as a function of ρ .
- HK: proved that a functional of ρ must exist.
- No guidance, though, as to what the functional should look like.
- Contrast between HF and DFT:
- HF **approximate** theory: solve the relevant equations **exactly**.
- DFT **exact** theory: solve the relevant equations **approximately** because the **form of the operator is unknown**.
- Exact DFT is variational. When approximations of E_{xc} are introduced, this is no longer true.
- Both exact and approximate DFT are size extensive.

Spin-polarized KS-DFT

- One of the nice features of DFT is the fact that there is a natural partitioning of alpha and beta spin electrons
 - The electron density already has this feature
- So... to handle open shell molecules, the unrestricted formalism provides the proper description.
 - No spin contamination
- There is no valid restricted open shell formalism.

Anatomy of a Functional

- Since there is no known exact forms for the exchange correlation functional, approximate forms have been determined
- Most functionals have a separate components for the exchange and correlation energy
- No systematic means for finding the exact functional
- Many have parameterized factors incorporated.

Local Density Approximation

- Uniform electron gas
- Functional of only the electron density
- Inaccurate for molecular systems
- Exchange: Slater
- Correlation: VWN

$$\varepsilon_x[\rho_\alpha, \rho_\beta] = -\frac{3}{2} \left(\frac{3}{4\pi}\right)^{1/3} (\rho_\alpha^{4/3} + \rho_\beta^{4/3})$$

$$VWN = \rho \varepsilon_c(x, \xi), \quad (A9)$$

where

$$\rho = \rho_\alpha + \rho_\beta, \quad x = \left(\frac{3}{4\pi\rho}\right)^{1/3}, \quad \xi = \frac{\rho_\alpha - \rho_\beta}{\rho}. \quad (A10)$$

The correlation potential is

$$\begin{aligned} \varepsilon_c(x, \xi) = & \varepsilon_c^F(x) + \varepsilon_c^A(x) g(\xi) \\ & \times \left[1 + \left[\frac{4}{9(2^{1/3}-1)} \frac{\varepsilon_c^F(x) - \varepsilon_c^A(x)}{\varepsilon_c^A(x)} - 1 \right] \xi^4 \right], \end{aligned} \quad (A11)$$

where

$$g(\xi) = \frac{2}{3} [(1+\xi)^{4/3} + (1-\xi)^{4/3} - 2], \quad (A12)$$

and the various ε_c have the form

$$\begin{aligned} \varepsilon_c(x) = & A \left[\ln \frac{x^2}{X(x)} + \frac{2b}{Q} \tan^{-1} \frac{Q}{2x+b} - \frac{bx_0}{X(x_0)} \left[\ln \frac{(x-x_0)^2}{X(x)} \right. \right. \\ & \left. \left. + \frac{2(2x_0+b)}{Q} \tan^{-1} \frac{Q}{2x+b} \right] \right], \end{aligned} \quad (A13)$$

Gradient Corrected Functionals

- Adding in the gradient of the density as a variable of the XC functional should give a more accurate description for molecular systems.
- Becke exchange functional (1988)
 - The B in all of the functionals
 - b determined only by computations on noble gases.

$$E_x[\rho(\mathbf{r})] = E_X^{LSDA}[\rho(\mathbf{r})] - b \sum_{\sigma=\alpha,\beta} \int \rho_\sigma^{(4/3)} \frac{x_\sigma^2}{1 + 6bx_\sigma \sinh^{-1} x_\sigma} d\mathbf{r}; \quad x_\sigma = \frac{|\nabla \rho_\sigma|}{\rho_\sigma^{4/3}}$$

- Combined with the other GGA correlation functionals to make complete XC functionals
 - BLYP, BPW91, etc...

Hybrid Functionals

- Self Interaction Error
 - The interaction of an electron with itself is fictitiously not zero when pure functionals are used
 - HF theory does not suffer from this problem
- Becke proposed a scheme in which so-called “exact” exchange could be incorporated into the functional form.
- The B3LYP functional

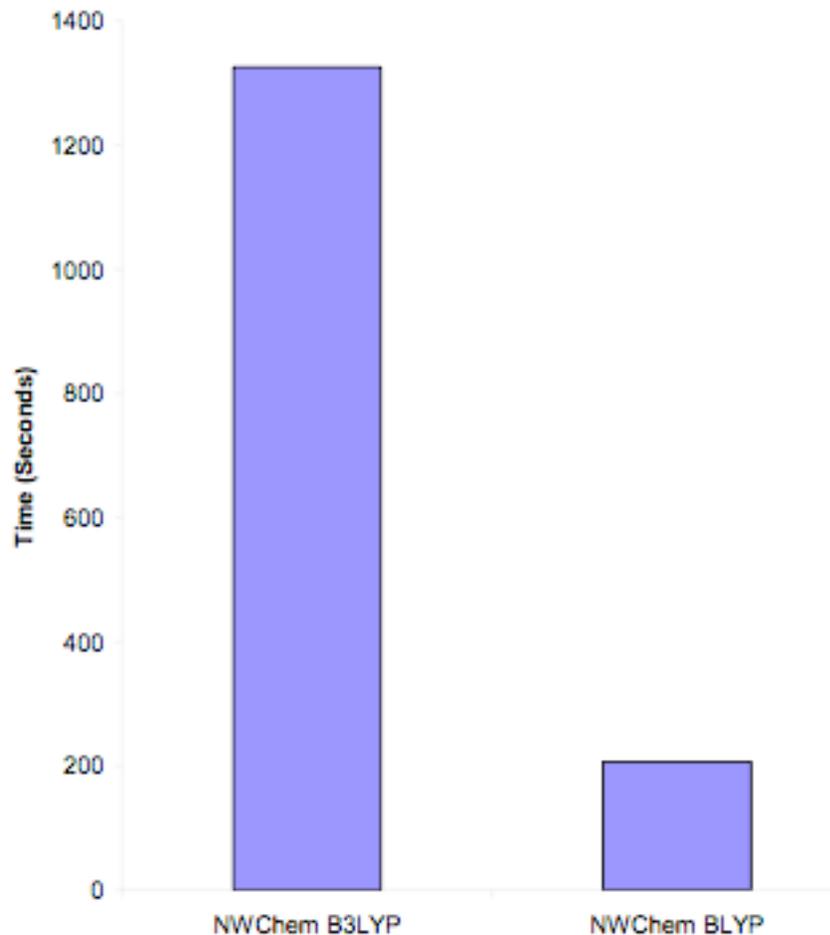
$$E_{XC}^{B3LYP} = (1 - a_0)E_X^{LSDA} + a_0E_X^{HF} + a_X \nabla E_X^{B88} + a_C E_C^{LYP} + (1 - a_C)E_C^{VWN}$$

- Generally the amount of “exact” exchange is determined through parameterization.
 - B3LYP, 56 atomization energies, 42 ionisation potentials, 8 proton affinities, and the total atomic energies of the ten first-row elements
- While “exact” exchange and HF exchange have the same form, they are not same thing.

Other functionals

- Taylor series expansion functions
 - HTCH, B97
 - Attempt to account for the incorrect asymptotic potentials in previous functionals.
 - Some are hybrid and some are pure.
- Meta-GGAs
 - Approximate exact exchange with functionals of the kinetic energy density.
 - Provide similar accuracy as hybrid functionals
- CAM functionals
 - Partition the Coulomb energy in to long and short range and treat each region differently

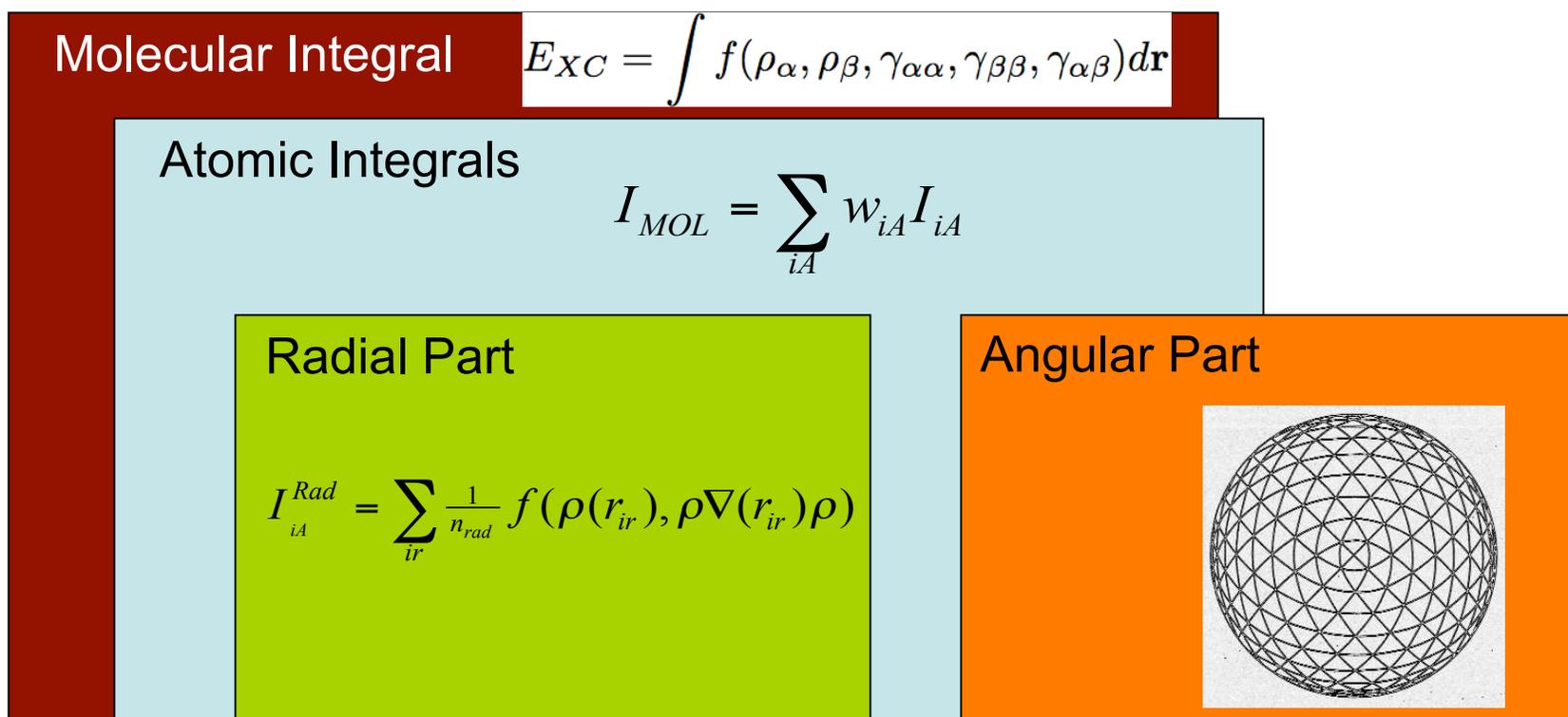
Hybrid functionals and efficiency



- Computing exact exchange is very inefficient
 - Has very non-local character
- When only the Coulomb energy needs to be computed, advanced techniques like Coulomb fitting, J-Engine, and CFMM can be used.
- This is why mGGA's are important.

Numerical Integration

- Generally, the integrals encountered in KS-DFT are of such a difficult nature that analytic solution is impossible.



Numerical Grids in DFT

- The performance and accuracy of DFT methods are intimately tied to the numerical integration grid.
 - Number of points, cutoffs, type of grid
- Pruned Grids
 - Vary the angular grid at different radial positions
 - Greatly reduces the number of points needed with little loss in accuracy
 - Gaussian's (75,302) pruned, SG-1

Accuracy

TABLE VIII. Errors evaluated with the 407 Set of contemporary functionals, using the TZ2P and cc-pVTZ basis sets.

Basis Set Functional	TZ2P			cc-pVTZ		
	rms energy	Gradient	Q_1	rms energy	Gradient	Q_1
HF	155	34.81	17917			
LSDA	105	15.93	7846			
PKZB	18.0	20.45	428.6			
PBE	20.7	15.68	426.0	20.5	16.42	449.5
mPW1K	16.8	19.18	399.6	17.7	18.27	483.2
PW91PW91	19.2	14.64	373.1	19.1	15.08	378.3
BP86	16.9	16.16	338.2	11.8	16.51	331.4
mPW91PW91	13.8	15.66	274.0	13.9	15.41	263.4
BLYP	9.8	18.50	249.7	11.0	18.91	283.9
BPW91	10.3	15.51	203.1	10.9	16.80	258.4
PBE0	11.9	11.19	199.8	12.2	12.05	219.8
OLYP	9.6	13.52	172.5	10.0	14.32	205.5
B98	8.7	13.40	166.2	8.9	13.39	175.7
B3LYP	9.6	11.36	165.3	10.2	11.62	177.3
B97-2	7.4	11.50	161.6	8.4	11.77	175.7
VSXC	9.4	11.39	158.6	9.4	11.43	167.5
HCTH/147	9.1	11.37	137.3	9.5	12.36	173.3
HCTH/407	8.0	11.28	135.3	9.3	12.46	187.6
HCTH/93	8.4	11.66	134.2	9.8	12.50	178.6
B97-1	7.3	10.81	130.9	8.1	11.19	143.7
τ -HCTH	7.3	10.65	114.2	8.4	11.72	150.4
τ -HCTH hybrid	6.3	10.36	107.5	7.3	11.11	133.2

A few more things to consider...

- The basis set dependence of DFT methods
 - GAP Project: 0.2eV agreement with experiment with DZP++ basis
 - Small basis, cancellation of errors
- Not just the relative energies
 - Potential energy surfaces of gas phase SN2 reactions have high amount of ionic character, and KS-DFT completely misses some transition states.
 - J. Phys. Chem. A, 105 (50), 11327 -11346, 2001

SCC-DFTB

- Modification of the original non-iterative DFTB approach to a second-order expansion of the charge density relative to a reference density.
- Slater-orbital basis used to expand the wavefunction
- Two-centered integrals are parameterized and pseudopotentials are used for core contributions.
- Mulliken charges are used to estimate the charge fluctuations

$$E_2^{TB} = \sum_i^{occ} \langle \Psi_i | H_0 | \Psi_i \rangle + 1/2 \sum_{\alpha, \beta}^N \gamma_{\alpha\beta} \Delta q_\alpha \Delta q_\beta + E_{rep}$$
$$\sum_{\nu}^M c_{\nu i} (H_{\mu\nu} - \varepsilon_i S_{\mu\nu}) = 0 \quad \forall \mu, i$$
$$H_{\mu\nu} = \langle \phi_\mu | \hat{H} | \phi_\nu \rangle + 1/2 S_{\mu\nu} \sum_{\zeta}^N (\gamma_{\alpha\zeta} + \gamma_{\beta\zeta}) \Delta q_\zeta, \quad \forall \mu \in \alpha, \nu \in \beta$$

Mean absolute errors (N comparisons) for a standard validation set of mostly organic compounds (C, H, N, O).

Property ^a	N	MNDO	AM1	PM3	OM1	OM2	OM3	DFTB
ΔH_f (kcal/mol)	140	6.3	5.5	4.2	3.5	3.1	2.9	7.7
R (pm)	242	1.4	1.7	1.1	1.2	1.6	2.0	1.5
θ (degree)	101	2.6	1.9	2.1	1.8	2.2	1.8	1.3
IP (eV)	52	0.46	0.35	0.42	0.32	0.26	0.45	3.82
μ (D)	53	0.35	0.26	0.27	0.25	0.28	0.27	0.37
ν (cm ⁻¹)	112	241	172	151	189	155	120	90

a) Heats of formation ΔH_f , bond lengths R, bond angles θ , vertical ionization potentials IP, dipole moments μ , vibrational wavenumbers ν .

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Programs available with DFT

- KS-DFT with numerical integrations with Gaussian basis sets
 - Gaussian, Q-Chem, NWChem, MPQC, GAMESS, Turbomol, Molpro, Jaguar, Spartan
- Planewave DFT codes
 - CPMD, CP2K, Qbox, LeanCP, PinyMD, VASP, Siesta
- Bottom line... lot's of codes, various features, try em out.

Other forms of DFT

- Plane-wave methods
- Carr-Parinello Dynamics
- QuickStep (available in CP2K)
 - Approximate local basis set with planewaves.
- LSMS
 - order N locally self-consistent multiple scattering (LSMS) DFT calculations
- TD-DFT
 - Time-dependent DFT for excited states