

Chemistry 137

Density Functional Theory
(largely unmodified from Berny
Schlegel – giving different
perspective)

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Electronic Energy Components

- Total electronic energy can be partitioned

$$E = E_T + E_{NE} + E_J + E_X + E_C$$

E_T = kinetic energy of the electrons

E_{NE} = Coulomb attraction energy between electrons and nuclei

E_J = Coulomb repulsion energy between electrons

E_X = Exchange energy, a correction for the self-repulsions of electrons

E_C = Correlation energy between the motions of electrons with different spins

- E_T , E_{NE} , & E_J are largest contributors to E
- $E_X > E_C$

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Electron Correlation

- In the Hartree-Fock approximation, each electron sees the average density (aka mean field) of all of the other electrons
- Two electrons cannot be in the same place at the same time
- Electrons must move to avoid each other, i.e. their motion is correlated
- Types of electron correlation
 - Dynamical
 - Non-dynamical
- The difference between the exact energy and the Hartree-Fock energy is the correlation energy for a particular basis set.

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Resources

- Cramer: Chapter 8 & Jensen: Chapter 6
- Scuseria and Staroverov, Theory and Applications of Computational Chemistry The First Forty Years, Chapter 24, **2005**.
- Kohn Nobel Lecture: Reviews of Modern Physics, 71, 1253, **1999**.
- Foresman and Frisch, Exploring Chemistry with Electronic Structure Methods, Appendix A
- Burke's DFT book (work in progress): <http://dft.rutgers.edu/kieron/beta/b4.pdf>
- Parr and Yang, Density Functional Theory, Oxford University Press, **1989**.

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Motivation

- The wave function itself is essentially uninterpretable.
- Reduce problem size: Wave functions for N -electron systems contain $4N$ coordinates.
- Wave function based methods quickly become intractable for large systems, even with continued improvement in computing power, due to the coupled motion of the electrons.
- A desire to work with some physical observable rather than probability amplitude.

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Thomas-Fermi-Dirac (TFD) Model

- Energy is a function of the one electron density, ρ
- Nuclear-electron attraction & electron-electron repulsion

$$E_{NE}[\rho] = \sum_A Z_A \int \frac{\rho}{r_A} d\tau \quad J[\rho] = \int \frac{\rho(1)\rho(2)}{r_{12}} d\tau_1 d\tau_2$$

- Thomas-Fermi approximation for the kinetic energy

$$T[\rho] = c \int \rho^{5/3} d\tau \quad c = \frac{3}{10} (3\pi^2)^{2/3}$$

- Slater approximation for the exchange energy

$$E_X[\rho] = c \int \rho^{4/3} d\tau \quad c = -\frac{9\alpha}{8} \left(\frac{3}{\pi} \right)^{1/3} \quad \alpha = 1$$

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X α Model

- TFD does not predict bonding and the total energies are in error by 15-50 %.
- If the α value in Slater's E_x is treated as parameter, then better results are achieved.
- The X α model (aka Hartree-Fock-Slater) uses $\alpha = 3/4$.
- Although X α has been superceded by modern functionals, it is still useful for inorganic systems and preliminary calculations.

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Theoretical Basis

- Hohenberg and Kohn (1964)
 - Energy is a functional of the density $E[\rho]$
 - The functional is universal, independent of the system
 - The exact density minimizes $E[\rho]$
 - Applies only to the ground state

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Constructing Density Functionals

- Exact form is unknown. Hohenberg-Kohn is only an existence proof.
- Density functionals have the form:

$$E[\rho] = (1-a)E_X^{\text{local}} + b\Delta E_X + aE_X^{\text{HF}} + (1-c)E_C^{\text{local}} + c\Delta E_C$$

- For LSDA: $a = b = c = 0$
- For Pure Functionals: $a = 0$
- Systematic improvement of functionals is possible, but complicated by the fact that exact constraints and properties of said functionals are still being elucidated.

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Type of Density Functionals

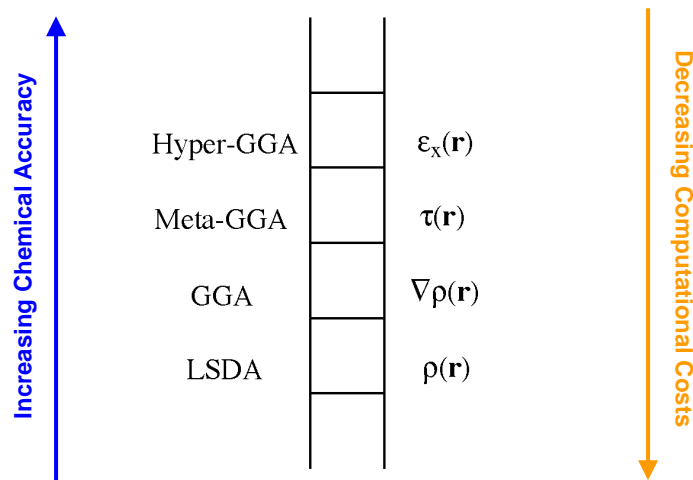
- Local spin density functionals (LSDA)
 - Depend only on the density
 - Derived for an electron gas, aka “jellium”

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Accuracy vs. Computational Cost

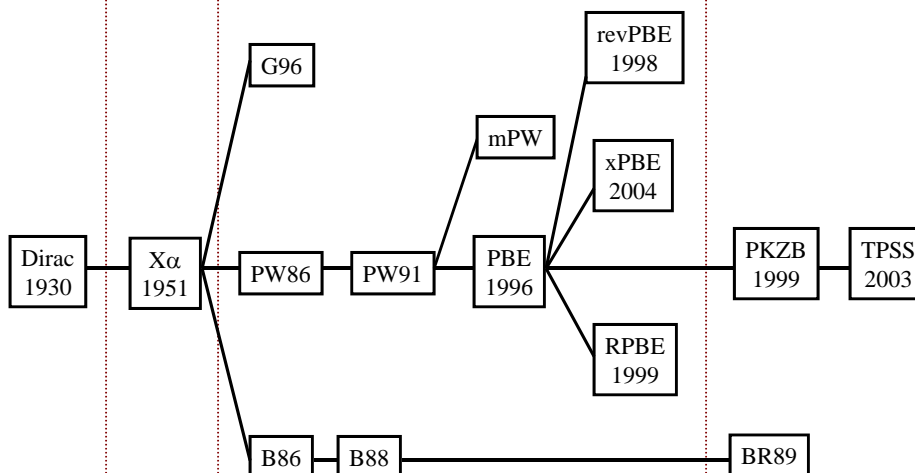


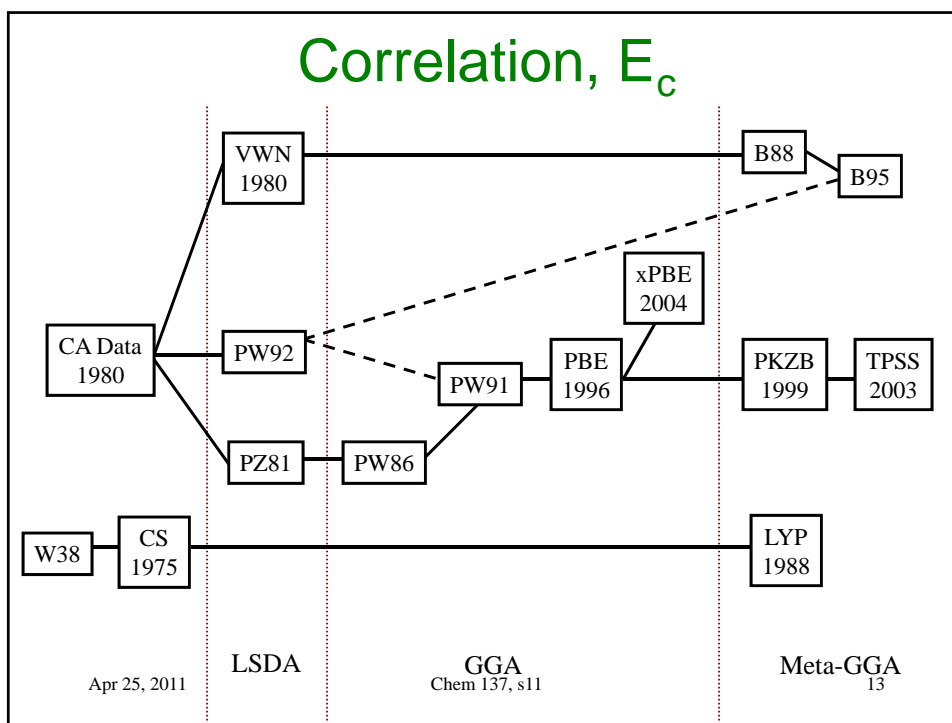
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Hartree World

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Exchange, E_x

LSDA
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Calculating E_{xc} Terms

- Exchange-correlation functionals must be numerically integrated
 - not as robust as analytic methods
- Energies and gradients are 1-3 times the cost of Hartree-Fock
- Frequencies are 2-4 times the cost of HF
- Some of this computational cost can be recuperated for pure density functionals by employing the density fitting approximation for the Coulomb interaction.

DFT Performance

- For accurate energies some exact exchange is needed, although systematically improved functionals such as TPSS do outperform hybrids.
- GGA functionals offer a major improvement over LSDA in terms of energetics. The improvement from GGA to Meta-GGA is not as large as that from LSDA to GGA.
- Open-shell DFT calculations are less prone to spin contamination.
- Multiconfigurational problems and van der Waals interactions are poorly described.

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DFT Literature

- Exchange-correlation hole density, $n_{xc}(r, r')$
 - describes how the presence of an electron at the point r depletes the total density of the other electrons at the point r' .
- Linear response function, $\chi(r, r'; \omega)$
 - describes the change of total density at the point r due to a perturbing potential at the point r' with a frequency ω .
- Energy density, ε_x or ε_c
 - energy density per particle

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DFT Strategies

- As usual, start with minimal or DZ basis sets before attempting very diffuse and polarized ones.
- For preliminary calculations or to clean up starting structures, use LSDA rather than HF. This is particularly important for metal containing systems.
- Optimize structures with a pure functional to benefit from the density fitting speedup.
- Pay attention to the $\langle S^2 \rangle$ value and run stability checks when necessary.
- If a tighter integration grid is required, optimize with the default grid, then re-optimize with the tighter grid.

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DFT in Gaussian

- The exchange and correlation functional must both be specified. **TPSSTPSS**
- Not all exchange and correlation functionals can be combined.
- LSDA functionals: **LSDA**, **SVWN5**, **XAlpha**
- Density fitting: **BLYP/Basis Set/Auto**
- SCF problems: **SCF=dsymm**
- Tighter integration grid:
Integral(Grid=Ultrafine)
- Stability checks: **Stable=Opt**

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- B86 - *J. Chem. Phys.*, 85, **1986**, 7184.
- B88c - *J. Chem Phys.*, 88, **1988**, 1053.
- B88x - *Phys. Rev. A.*, 38, **1988**, 3098.
- B95 - *J. Chem. Phys.*, 104, **1996**, 1040.
- BR89 - *Phys. Rev. A.*, 39, **1989**, 3761.
- G96 - *Mol. Phys.*, 89, **1996**, 433.
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- mPW - *J. Chem. Phys.*, 108, **1998**, 664.
- PBE - *Phys. Rev. Lett.*, 77, **1996**, 3865.
- PKZB - *Phys. Rev. Lett.*, 82, **1999**, 2544.
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- PW91 - *Phys. Rev. B.*, 46, **1992**, 6671.
- PW92 - *Phys. Rev. B.*, 45, **1992**, 13244.
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- TPSS - *Phys. Rev. Lett.*, 91, **2003**, 146401.
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- W38 - *Trans. Faraday Soc.*, 34, **1938**, 678.
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- X α - *Phys. Rev.*, 81, **1951**, 385.

Density Functional Literature References

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