Density Functional Theory

Fundamentals

Video V.i

Chemistry Department Seminar

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Density Functional Theory: New Developments

Donald G. Truhlar
Department of Chemistry, University of Minnesota

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Why is electronic structure theory important?

Most of the information we want to know about chemistry is in the electron density and electronic energy.

dipole moment,
charge distribution,
...

Born-Oppenheimer
approximation 1927

potential energy surface

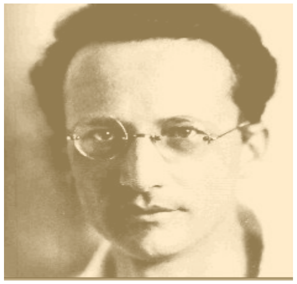
molecular geometry
bond energies

barrier heights
spectra

How do we calculate the electronic structure?

Example: electronic structure of benzene (42 electrons)

Erwin Schrödinger 1925 — wave function theory



All the information is contained in the wave function, an antisymmetric function of 126 coordinates and 42 electronic spin components.

THE QUANTUM NIGHTMARE

$$\boxed{\begin{aligned} H\Psi &= E\Psi = \sum_{i=1}^{N}\Big(\frac{-\hbar^2}{2m}\nabla_i^2\Psi \\ &- Ze^2\sum_{\mathbf{R}}\frac{1}{|\mathbf{r_i}-\mathbf{R}|}\Psi\Big) \\ &+ \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r_i}-\mathbf{r_j}|}\Psi \end{aligned}}$$

- The red term describes correlation and is very difficult to account for
- The Hamiltonian can be generalised:

$$\boxed{H = T + V + U}$$

where U is the mutual interaction energy of the electrons and $V = \sum_{i=1}^{N} v(\mathbf{r}_i)$, the interaction with an arbitary external field.

Theoretical Musings

- Ψ is complicated.
- Difficult to interpret.
- Can we simplify things?
- Ψ has strange units: (prob. density)$^{1/2}$,
- Can we not use a physical observable?
- What particular physical observable is useful?
- Physical observable that allows us to construct the Hamiltonian a priori.

How do we calculate the electronic structure?

Example: electronic structure of benzene (42 electrons)

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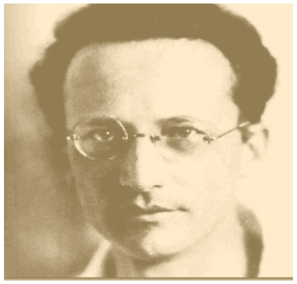


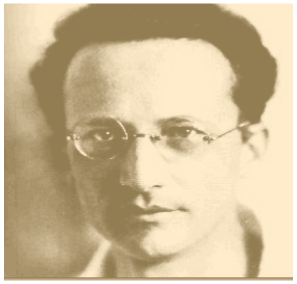
All the information is contained in the wave function, an antisymmetric function of 126 coordinates and 42 electronic spin components.

Pierre Hohenberg and Walter Kohn 1964 — density functional theory

All the information is contained in the density, a simple function of 3 coordinates.

Electronic structure (continued)

Erwin Schrödinger 1925 — wave function theory



Nobel Prize in Physics 1933

Walter Kohn 1964 and continuing work — density functional theory

Nobel Prize in Chemistry 1998
(with John Pople, for *practical* WFT)

How do we do the calculation?

wave function theory

$$H\Psi = E\Psi$$

$$E = \min_{\Psi} \left\langle \Psi \middle| H \middle| \Psi \right\rangle$$

$\Psi \equiv$ trial wave function

density functional theory

$$E = \min_{n} \left\{ \int V_{\text{nuclei}}(\vec{r})\, n(\vec{r})\, d^3\vec{r} + F\left[n(\vec{r})\right] \right\}$$

$n \equiv$ trial density; $F \equiv$ universal functional

What’s the problem?

wave function theory

$$H\Psi = E\Psi$$

Paul Dirac 1929: “the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”

density functional theory

$$E = \min_n \left\{ \int V_{\text{nuclei}}(\vec{r})n(\vec{r})d^3\vec{r} + F[n(\vec{r})] \right\}$$

We do not even have an equation for *F*!

Density Functional Theory

Early Approximations

Video V.ii

On what does H depend?

- Position and atomic number of the nuclei.
- Total number of electrons, N.
- A good physical observable: the electron density
- Number of electrons per unit volume in a given state is the electron density for that state.

$$\rho(\mathbf{r}) = N \int \dots \int \Psi(\mathbf{r}, x_{2,} \dots, x_N) \Psi(\mathbf{r}, x_{2,} \dots, x_N) dx_2 \dots dx_N$$

- ρ integrated over all space gives N:

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

- The nuclei are effectively point charges:
- Their positions correspond to local maxima in the electron density
- Maxima are also cusps.

Intuitive Apparent Equivalence

- Assignment of the nuclear atomic numbers.
- The atomic number can be obtained from the electron density.
- For any nucleus A located at an electron density maximum r_A

$$\left.\frac{\partial\bar{\rho}(r_A)}{\partial r_A}\right|_{r_A=0} = -2Z_A\rho(r_A) \qquad (1)$$

- Z_A: atomic number of A, r_A radial distance from A,
- $\bar{\rho}(r_A)$ spherically averaged density
- Of course, we do not yet have a simple formalism for finding the energy.
- But, given a known density, one could form the Hamiltonian operator, solve the Schrödinger equation and determine the wave functions and energy eigenvalues.

Early Approximations

- Energy is separable into kinetic and potential components.
- Use only the electron density to determine the molecular energy: consider the system as classical:
- easy to determine the components of the potential energy.
- Nuclear-electron attraction

$$V_{ne}\left[\rho(r)\right] = \sum_{k}^{nuclei} \int \frac{Z_k}{\left|r - r_k\right|}\rho(r)\,dr \qquad (2)$$

- Self-repulsion of a classical charge distribution

$$V_{ee}\left[\rho(r)\right] = \frac{1}{2}\int\int \frac{\rho(r_1)\rho(r_2)}{\left|r_1 - r_2\right|}\,dr_1 dr_2 \qquad (3)$$

- r_1, r_2 dummy integration variables running over all space.

Thomas-Fermi Kinetic Energy I

- Kinetic energy of a continuous charge distribution.
- Introduce a fictitious substance “Jellium”: infinite number of electrons moving in an infinite volume of space with uniformly distributed positive charge.
- Also called uniform electron gas (ueg): constant non-zero density.
- Thomas and Fermi (1927) used fermion statistical mechanics to derive the kinetic energy for ueg as particles in a box

$$T_{ueg}\left[\rho(r)\right] = \frac{3}{10}\left(3\pi^2\right)^{2/3}\int \rho^{5/3}(r)dr \qquad (4)$$

- T, V are functions of the density, while the density is a function of three spatial coordinates.
- A function whose argument is itself a function is called a “functional”.
- T, V are density functionals.

Thomas-Fermi Model

- TF equations together with an assumed variational principle, represent the first effort to define a Density Functional Theory.
- Energy is computed with no reference to the wave-function.
- No use in modern quantum chemistry: all molecules unstable relative to dissociation into atoms.
- Huge approximation in (3) for the interelectronic repulsion: it ignores the energetic effects associated with correlation and exchange.
- Hole function: *h* corrects for the energetic errors introduced by assuming a classical behaviour.

$$\left\langle \Psi \left| \sum_{i<j}^{N} \frac{1}{r_{ij}} \right| \Psi \right\rangle = \frac{1}{2} \int\int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 + \frac{1}{2} \int\int \frac{\rho(r_1) h(r_1;r_2)}{|r_1 - r_2|} dr_1 dr_2 \qquad (5)$$

Hole Function I

$$\left\langle \Psi \left| \sum_{i<j}^{N} \frac{1}{r_{ij}} \right| \Psi \right\rangle = \frac{1}{2}\int\int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 + \frac{1}{2}\int\int \frac{\rho(r_1)h(r_1;r_2)}{|r_1 - r_2|} dr_1 dr_2 \qquad (5)$$

- LHS of (5) is the exact QM interelectronic repulsion.
- Second term on RHS corrects for the errors in the first term (the classical expression).
- Hole function h associated with ρ is centred on the position of electron 1 and is evaluated from there as a function of the remaining spatial coordinates defining r_2.
- The value and form of *h* varies as a function of r_2 for a given value of r_1.
- One electron system: LHS of (5) must be zero.
- First term of RHS of (5) is not zero since $\rho \geq 0$ throughout space.

Hole Function II

- In the one-electron case h is simply the negative of the density.
- In the many-electron case: exact form of h can rarely be established.
- h *both* corrects for self-interaction error (SIE) *and* accounts for exchange and correlation energy in a many-electron system.

Slater Exchange I

- HF by construction avoids SIE and exactly evaluates the exchange energy (correlation is a problem, though).
- Slater (1951): one of the consequences of the Pauli principle is that the Fermi exchange hole** is larger than the correlation hole.
- Exchange corrections to classical interelectronic repulsion larger than correlation corrections (one or two order of magnitude).
- Slater decided to ignore correlation corrections, and simplify the exchange corrections.
- **:Consequence of the Pauli exclusion principle. Reduced probability of finding two electrons of the same spin close to one another. Fermi hole surrounds each electron.

Slater Exchange II

- Exchange hole about any position: sphere of constant potential; radius depending on the magnitude of the density at that position.
- With this approximation the exchange energy is

$$E_x = \frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{1/3}\int \rho^{4/3}(r)dr \qquad (6)$$

- In the Slater derivation: α=1.
- Eq. (6): Slater exchange.

Unit analysis challenge: Satisfy yourself that 4/3 is the proper exponent on the density in order to compute an energy. What about eq. 4 earlier? Is 5/3 correct for kinetic energy?

Xα

- Many early workers saw fit to treat alpha as an empirical value.
- HF calculations employing eq (6) instead of doing exchange "properly" called Xα (or Hartree-Fock-Slater (HFS)).
- Empirical analysis in a variety of systems suggested that $\alpha=3/4$ provides more accurate results than $\alpha=1$ or $\alpha=2/3$.
- DFT (and HFS) models up to this point gave generally large errors in molecular calculations and had relatively little impact on chemistry, although the physics community found them useful because their "locality" facilitates, say, solid-state calculations.

Density Functional Theory

Hohenberg-Kohn Theorems

Video V.iii

Rigorous Foundation

- Hoenberg and Kohn (1964) proved two theorems which establish DFT as a rigorous quantum chemical methodology.
- Electrons interact with one another and with an external potential.
- Hohenberg-Kohn theorem employs the ground-state density.
- External potential is the attraction to the nuclei.
- Integration of the density: number of electrons.
- It remains to determine the external potential for the real system (charges and positions of the nuclei).
- The ground-state density uniquely determines the external potential.
- Proof proceeds via *reductio ad absurdum*.

Hohenberg Kohn Theorem I

- Assume that two different external potentials can each be consistent with the same non-degenerate ground-state density ρ_0.
- Call potentials: v_a and v_b.
- Potentials determine Hamiltonians H_a and H_b.
- Associate with each H_a and H_b a ground-state wave function Ψ_0 and eigenvalue E_0.
- Variational theorem: the expectation value of H_a over the wf b must be higher than the ground-state energy of a.

$$E_{0,a} < \left\langle \Psi_{0,b} \middle| H_a \middle| \Psi_{0,b} \right\rangle \quad (7)$$

Hohenberg Kohn Theorem I

$$
\begin{aligned}
E_{0,a} &< \left\langle \Psi_{0,b} \middle| H_a - H_b + H_b \middle| \Psi_{0,b} \right\rangle \\
&< \left\langle \Psi_{0,b} \middle| H_a - H_b \middle| \Psi_{0,b} \right\rangle + \left\langle \Psi_{0,b} \middle| H_b \middle| \Psi_{0,b} \right\rangle \\
&< \left\langle \Psi_{0,b} \middle| v_a - v_b \middle| \Psi_{0,b} \right\rangle + E_{0,b} \qquad (8)
\end{aligned}
$$

- Potentials v are one-electron operators:
- Last line of (8) can be written in terms of the ground state density:

$$E_{0,a} < \int \left[v_a(r) - v_b(r) \right] \rho_0(r) dr + E_{0,b} \qquad (9)$$

- No distinction between a and b, we can interchange the indices in (9)

$$E_{0,b} < \int \left[v_b(r) - v_a(r) \right] \rho_0(r) dr + E_{0,a} \qquad (10)$$

Hohenberg Kohn Theorem I

- Add (9) and (10):

$$
\begin{aligned}
&E_{0,a} + E_{0,b} < \\
&\int \left[v_b(r) - v_a(r) \right] \rho_0(r) dr + \int \left[v_a(r) - v_b(r) \right] \rho_0(r) dr \\
&+ E_{0,b} + E_{0,a} \\
&\qquad < E_{0,b} + E_{0,a} \qquad (11)
\end{aligned}
$$

- assumption that the ground state densities associated with the wave functions a and b are the same permits us to eliminate the integrals as they must sum to zero.
- Impossible result: our initial assumption was incorrect.

Hohenberg Kohn Theorem I

- The non-degenerate ground-state density must determine the external potential ⟶ Hamiltonian ⟶ wave function.
- H determines not just the ground-state wave function, but all excited-state wave functions.
- What utility are the densities of the excited states?
- HK theorem can be extended to the lowest energy (non-degenerate) state within each irrep of the molecular point group.

Hohenberg Kohn Theorem II

- Theorem I: existence theorem.
- How to *get* the density of a system?
- Just as with MO theory: need a way to optimize the energy.
- HK II theorem: the density obeys a variational principle.
- Have some well-behaved density: integrate to the proper number of electrons N.
- Theorem I: this density determines a candidate wave function Ψ_{cand}
- Energy expectation value:

$$\left\langle \Psi_{cand} \middle| H_{cand} \middle| \Psi_{cand} \right\rangle = E_{cand} \geq E_0 \qquad (12)$$

Hohenberg Kohn Theorem II cont.

- In principle: choose different densities and those that provide the lower energies are closer to correct.
- How do we choose improved densities?
- We want to avoid solving the Schrödinger equation.
- How can the density be used in a variational equation to determine the energy without recourse to the wave function?

Density Functional Theory

Kohn-Sham (KS) Theory

Video V.iv

Kohn-Sham Self-consistent field

- Trick: Take a fictitious system of non-interacting electrons where ground-state density is the same density as the *real* system where the electrons interact.
- Real and fictitious system have the same positions and atomic numbers of the nuclei (same density)
- An easy Hamiltonian: a sum of one-electron operators.
- Eigenfunctions: Slater determinants of the individual one-electron eigenfunctions (cf. text, Section 4.5.1).
- Eigenvalues: sum of one-electron eigenvalues (cf. text, Section 4.5.1).

Kohn-Sham Density Functional Theory

1965

Consider the electronic energy of a molecule:

$$E = T + V_{\mathrm{ne}} + V_{\mathrm{ee}} + V_{\mathrm{xc}}$$

Noninteracting kinetic energy

Coulomb interaction with nuclei

Coulomb interaction of electron density ρ with itself

Write density as a product of orbital densities; compute T from orbitals.

🚩

Electron cannot interact with itself.

Kohn-Sham Self-consistent field

- Divide energy functional into specific components

$$E[\rho(r)] = T_{ni}[\rho(r)] + V_{ne}[\rho(r)] + V_{ee}[\rho(r)] + \Delta T[\rho(r)] + \Delta V_{ee}[\rho(r)] \qquad (13)$$

- T_{ni}: kinetic energy of non-interacting electrons
- V_{ne}: nuclear-electron interaction
- V_{ee}: classical electron-electron repulsion
- ΔT: correction to kinetic energy
- ΔV_{ee}: all non-classical corrections to el.-el. repulsion energy

KS SCF II

- Express the density in an orbital basis set:

$$E\left[\rho(r)\right]=\sum_{i}^{N}\left(\langle\chi_i|-\frac{1}{2}\nabla_i^2|\chi_i\rangle-\langle\chi_i|\sum_{k}^{nuclei}\frac{Z_k}{|r_i-r_k|}|\chi_i\rangle\right) \qquad (14)$$

$$+\sum_{i}^{N}\langle\chi_i|\frac{1}{2}\int\frac{\rho(r')}{|r_i-r'|}dr'|\chi_i\rangle+E_{xc}\left[\rho(r)\right]$$

- N: number of electrons.
- Density for a Slater determinantal wf (exact for the non-interacting system)

$$\rho(\mathbf{r})=\sum_{i=1}^{N}|\chi_i(\mathbf{r})|^2 \qquad (15)$$

Simplest functional: LSDA

local spin-density approximation

Kohn & Sham 1965, von Barth & Hedin 1972

Example: for a closed-shell system:

$$\text{Energy} = T_{\text{KS}} + V_{\text{en}} + V_{\text{ee}} + \int d^3\vec{r}\,\rho(\vec{r})\left\{\varepsilon_x[\rho(\vec{r})] + \varepsilon_c[\rho(\vec{r})]\right\}$$

density

Exchange energy
of <u>uniform electron gas</u>
neutralized by uniform
positive background charge

$= -0.73856\,\rho^{1/3}$ (from Dirac $\alpha = 2/3$)

Correlation energy.
Fit to Monte Carlo
calculations for
<u>uniform electron gas</u>

KS SCF III

- Difficult terms ΔT and ΔV_{ee} are contained in:
- E_{xc}: exchange-correlation energy. It includes:

  1) effects of quantum mechanical exchange and correlation

  2) correction for the classical self-interaction energy

  3) difference in kinetic energy between the non-interacting system and the real one
- Find orbitals χ that minimize E in (13). They satisfy:

$$h_i^{KS}\chi_i = \varepsilon_i \chi_i \qquad (16)$$

- KS operator is one-electron operator!

$$h_i^{KS} = -\frac{1}{2}\nabla_i^2 - \sum_k^{nuclei} \frac{Z_k}{|r_i - r_k|} + \int \frac{\rho(r')}{|r_i - r'|} dr' + V_{xc} \qquad (17)$$

KS SCF IV

- Where:
$$V_{xc} = \frac{\partial E_{xc}}{\partial \rho} \qquad (18)$$

- V_{xc} is a functional derivative. One-electron operator for which the expectation value of the KS Slater determinant is E_{xc}.

- Since *E* (eq (13)) is exact, the orbitals $\{\chi\}$ must provide the exact density (the minimum must correspond to the real system).

- These orbitals also form the Slater-determinantal wave function for the separable non-interacting Hamiltonian h_i^{KS}
$$\sum_{i=1}^{N} h_i^{KS} \left| \chi_1 \chi_2 \cdots \chi_N \right\rangle = \sum_{i=1}^{N} \varepsilon_i \left| \chi_1 \chi_2 \cdots \chi_N \right\rangle \qquad (19)$$

KS SCF V

- Use the first term on the r.h.s. of (14) to compute the kinetic energy of the non-interacting electrons.
- To determine the KS orbitals use the same approach as in MO theory:
- Express KS orbitals within a set of basis functions {ϕ}, determine the individual orbital coefficients by solution of a secular equation entirely analogous to that employed in the HF theory.
- Replace the $F_{\mu\nu}$ elements by the the $K_{\mu\nu}$ elements

$$K_{\mu\nu} = \left\langle \phi_\mu \middle| -\frac{1}{2}\nabla^2 - \sum_k^{nuclei} \frac{Z_k}{|r - r_k|} + \int \frac{\rho(r')}{|r - r'|} dr' + V_{xc} \middle| \phi_\nu \right\rangle \qquad (20)$$

HF vs DFT I

Similarities between HF and KS

- Common variational principle
- Kinetic energy and nuclear attraction component of matrix elements of **K** are identical to those of **F**.
- If the density in the *classical* interelectronic repulsion operator is expressed in the same basis functions used for the KS orbitals, then the same four-index electron-repulsion integrals will appear in **K** as in **F**.
- Density required for computation of the secular matrix elements.
- Density determined using the orbitals obtained from the solution of the secular equation:
- KS procedure is a SCF iterative procedure.
- Historically: modify existing codes for HF calculations to perform DFT calculations.

HF vs DFT II

Key differences between HF and KS

- 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.

Density Functional Theory

Kohn-Sham (KS) Theory
Local (Spin) Density Approximation

Video V.v

Exchange-correlation Energy

- E_{xc}: difference between the classical and quantum mechanical el.-el. repulsion.
- It *also* includes the difference in kinetic energy between the fictitious non-interacting system and the real system.
- Most functionals do not attempt to compute the K.E. correction explicitly.
- Either they ignore the term, or construct a hole function analogous to that of eq. (5) that also incorporates the kinetic energy difference between the interacting and non-interacting systems, perhaps empirically.

Exchange-correlation (xc) Functionals

- In many functionals, empirical parameters introduce some kinetic energy correction based on experiment.
- Common notations in the field follow
- Functional dependence of E_{xc} on ρ expressed as an interaction between ρ and an energy density, that is itself dependent on the electron density

$$E_{xc}\left[\rho(r)\right] = \int \rho(r)\varepsilon_{xc}\left[\rho(r)\right]dr \quad (21)$$

xc Functionals II

- Energy density ε_{xc} is treated as a sum (separable or not) of individual exchange and correlation contributions.
- Slater (or Dirac, or empirical [α]) exchange energy density:

$$\varepsilon_x\left[\rho(r)\right] = -\frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{1/3}\rho^{1/3}(r) \quad (22)$$

- Electron density can also be expressed in terms of an effective radius such that exactly one electron would be contained within the sphere defined by that radius were it to have the same density throughout as its center

$$r_S(r) = \left(\frac{3}{4\pi\rho(r)}\right)^{1/3} \quad (23)$$

xc Functionals III

- Spin not considered so far.
- Use individual functionals of the α and β densities.
- Spin density at any position is expressed in terms of the normalized spin polarization:

$$\zeta(r) = \frac{\rho^{\alpha}(r) - \rho^{\beta}(r)}{\rho(r)} \quad (24)$$

- α spin density is one-half of the product of the total ρ and (ζ +1) and the β spin density is the difference between the total rho and that value.

Local Density Approximation

- LDA: any DFT where the value of ε_{xc}, at some position r, can be computed exclusively from the value of ρ at that position, i.e., the 'local' value of ρ.
- Functionals derived primarily from the uniform electron gas (uniform density at every position in space).
- L(S)DA implies that it is the UEG exchange and correlation functionals that are employed for molecular calculations.
- Can be extended to spin-polarized cases (z from eq. (24), "0" and "1" refer to "no-spin" and "all-same-spin" UEG).

$$\varepsilon_x\left[\rho(r),\zeta(r)\right]=\varepsilon_x^0\left[\rho(r)\right]+$$

$$\left\{\varepsilon_x^1\left[\rho(r)\right]-\varepsilon_x^0\left[\rho(r)\right]\right\}\left[\frac{(1+\zeta)^{4/3}+(1-\zeta)^{4/3}-2}{2\left(2^{1/3}-1\right)}\right] \quad (25)$$

Local Density Correlation

- Correlation energy: no analytical derivation of this functional has proven possible.
- Quantum Monte Carlo: Ceperley and Alder (1980) computed the total energy for fully interacting uniform electron gases of various densities.
- Subtract the analytical exchange energy to determine the correlation energy.
- Vosko, Wilk and Nusair (1980): designed local functionals of the density fitting to these results.
- Spin-polarized functional analogous to (25), but with the unpolarized and fully polarized correlation energy densities.

Local Density Correlation

- Different sets of empirical constants.
- VWN: several fitting schemes varying the functional forms.
- LSDA that employs a combination of Slater exchange and the VWN correlation energy expression: SVWN.
- Correlation energy functional is very complex.
- DFT methods are often semiempirical: they include empirically optimized constants and functional forms.
- Solution of E_{xc} integrals typically not possible analytically.
- Evaluation of integrals involving exchange and correlation energy densities in DFT is done numerically on a grid.
- Use of efficient quadrature schemes.
- In modern codes: default grid unless otherwise specified by the user.

KS-SCF Procedure

- In HF theory: Number of Coulomb integrals requiring evaluation is N^4.
- In DFT it can be reduced to N^3, N number of KS AO basis functions.
- After basis set and molecular geometry choice, the overlap integrals, kinetic-energy, and nuclear-attraction integrals are computed. Same in HF and DFT
- HF: construct a density matrix and then compute the two-electron integrals: Coulomb and exchange.
- DFT: construct a density matrix and also construct V_{xc}
- Evaluate the remaining integrals in each KS matrix element.
- After this point KS and HF SCF are identical.

KS-SCF Procedure II

- New orbitals are determined from solution of the secular equation.
- Density is determined from these orbitals and compared with density of the previous iteration.
- When SCF procedure is converged: compute the energy by using the final density plugged into eq (14).
- Cf. HF, where the energy is evaluated as the expectation value of the H operator acting on the HF Slater determinant.
- Geometry optimization? Determine whether the structure corresponds to a stationary point.
- Using the LSDA approximation means that:
- The exchange-correlation energy density at every position in space for the molecule is the same as that for the uniform electron gas having the same density as is found at that position.

LSDA enjoyed early success in physics.

The local spin-density approximation "gives bond lengths and thus the geometries of molecules and solids typically with an astonishing accuracy of ~1%."

– *W. Kohn (Nobel lecture, 1998)*

But LSDA molecular *energies* have systematic errors.

In rest of lecture: Results are given for representative or large databases and reasonable basis sets; details in papers.

Mean (unsigned) errors in kcal/mol

	MAIN-GROUP	
	bond energies	barrier heights
Hartree-Fock theory	31	9
Local spin-density approximation	16	18

Density Functional Theory

Kohn-Sham (KS) Theory
Generalized Gradient Approximation

Video V.vi

Next step: add gradient dependence.

Local spin-density approx. $$F^{\text{LSDA}} = F\left[\rho(\mathbf{r})\right]$$

Gradient expansion $$F = F^{\text{LSDA}}\left[1 + \mu s^2 + \text{higher - order}\right]$$

$$s \equiv \text{constant } \times \frac{|\nabla\rho|}{\rho^{4/3}}$$

known: Antoniewicz &
Kleinman 1985

Later slide: a second order method with this correct μ

↓

SOGGA

Density Gradient Corrections

- In a molecule the electron density is not spatially uniform.
- LDA has serious limitations for energies, although it gives good geometries.
- Improve functionals by making them depend on the extent to which the density is locally changing, i.e. the gradient of the density.
- Functionals that depend on both the density and the gradient of the density: gradient corrected or generalized gradient approximation (GGA) functionals.
- Most GGA functionals are constructed with the correction being a term added to the LDA functional

$$\varepsilon_{x/c}^{GGA}\left[\rho(r)\right]=\varepsilon_{x/c}^{LSD}\left[\rho(r)\right]+\Delta\varepsilon_{x/c}\left[\frac{\left|\nabla\rho(r)\right|}{\rho^{4/3}(r)}\right] \quad (28)$$

verify that this term is dimensionless

- x/c: same functional for either exchange or correlation.
- The dependence of the correction term is on the dimensionless reduced gradient.

Density Gradient Corrections II

- Most popular GGA exchange functional to date: Becke 1988 (B). (*23,000+ citations in March 2013*)
- Correct asymptotic behaviour at long range for the energy density and incorporates a single empirical parameter.
- Value of the parameter optimized by fitting to the exactly known exchange energies of six noble gas atoms (from He to Rn).
- Other exchange functionals similar to Becke: CAM(B), PW, FT98, mPW.
- Alternative GGA exchange functionals have been developed based on a rational function expansion of the reduced gradient. They contain no empirically optimized parameters: B86, P, PBE.
- Correlation functionals: P86 (Perdew 1986); PW91 (Perdew Wang 92).
- LYP correlation: (Lee, Yang, Parr 1988) does not correct the LDA expression but computes the full correlation energy.
- It contains four empirical parameters fit to helium atom. It is a correlation functional that provides an exact cancellation of the self-interaction error in one-electron systems.

Progress: GGAs

$$F^{\text{GE}} = F^{\text{LSDA}}(\rho)\left[1+\mu s^2 + \text{higher - order}\right] \qquad s \equiv \text{constant} \times \frac{|\nabla\rho|}{\rho^{4/3}}$$

correct $\mu = 0.1235$: “Gradient expansion”

$$F^{\text{GGA}} = F(\rho, s)$$

incorrect μ : “Generalized gradient approximation” ≡ GGA

Examples: BLYP (1988) $\mu = 0.2743$

PBE (1996) $\mu = 0.2195$

Generalized gradient approximation shows promise.

	Mean (unsigned) errors in kcal/mol	
	Bond energies	Barrier heights
Hartree-Fock theory	31	9
Local spin-density approximation	16	18
Correct thru 2nd order: SOGGA	7	13
GGA: BLYP (1988)	1.5	8

BLYP ↔ Becke-Lee-Yang-Parr

This aroused the attention of many quantum chemists.

Density Gradient Corrections III

- Taylor-function-expansion justification for the importance of the gradient.
- “Obvious” next step: include second derivative of the density, i.e. the Laplacian.
- Becke and Rousell proposed an exchange functional (BR).
- Proynov, Salahub, and co-workers examined the same idea for the correlation functional (Lap).
- Meta-GGA because they go beyond the gradient correction.
- Alternative Meta-GGA formalism, numerically more stable is to include in the exchange-correlation potential a dependence on the kinetic-energy density τ:

$$\tau(r) = \sum_{i}^{occ} \frac{1}{2} \left| \nabla \psi_i(r) \right|^2 \quad (29)$$

- Functions ψ are the self-consistently determined KS orbitals.
- Some examples of MGGA functionals for exchange, correlation, or both, are B95, B98, ISM, τHCTH, and the Minnesota local functionals M06-L and M11-L.
- Cost of MGGA comparable to that for GGA. MGGA generally more accurate than GGA.

Density Functional Theory

Kohn-Sham (KS) Theory
Adiabatic Connection (Hybrid Functionals)

Video V.vii

Adiabatic Connection Methods

- Posits controlling the amount of electron-electron interaction in a many-electron system.
- A switch that smoothly converts the non-interacting KS reference system to the real, interacting system.
- Thus, clearly the exchange-correlation energy can be computed as

$$E_{xc} = \int_0^1 \langle \Psi(\lambda) | V_{xc} | \Psi(\lambda) \rangle d\lambda \quad (30)$$

- Where lambda describes the extent of interelectronic interaction: 0 (none) to 1(exact).

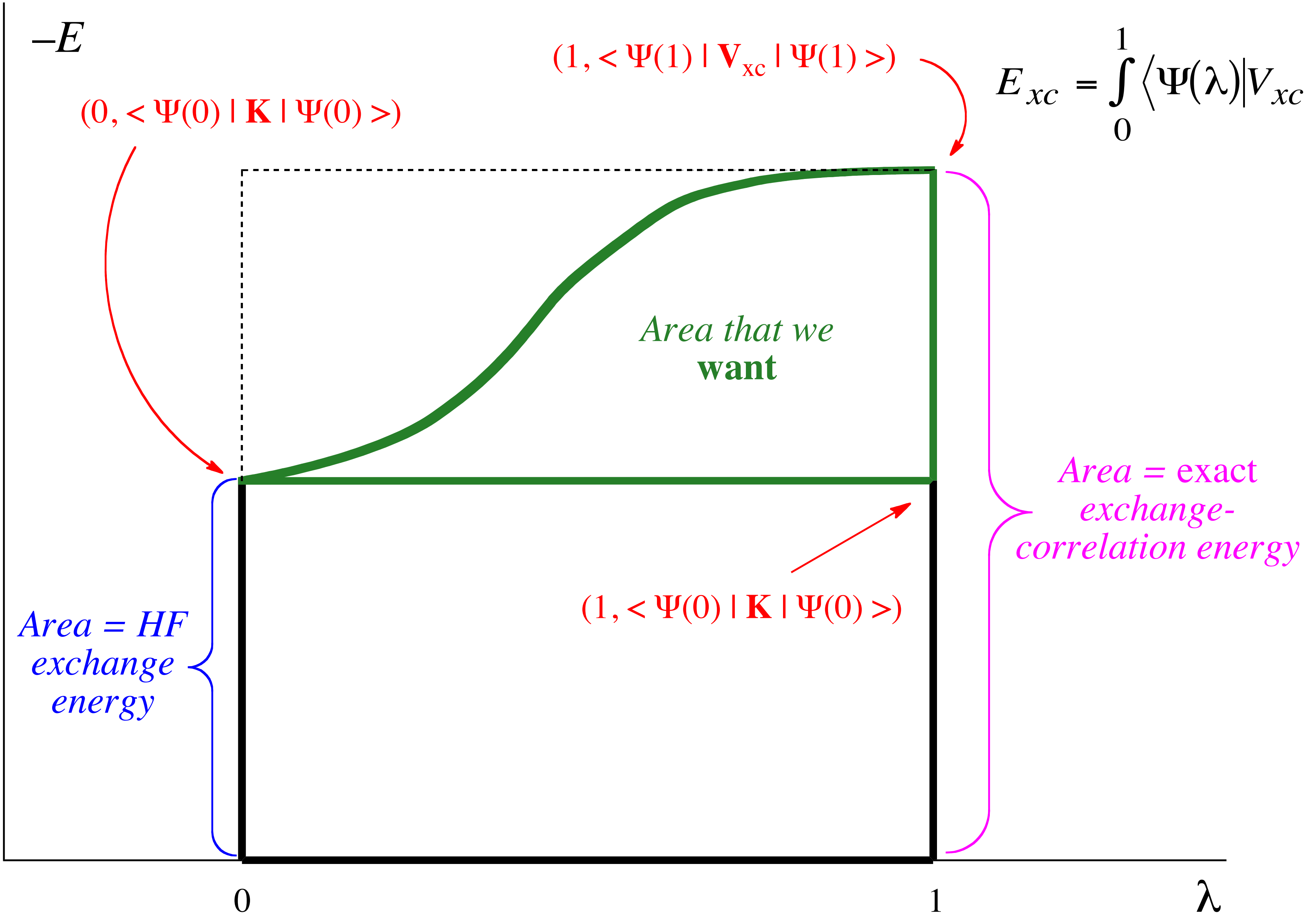
Adiabatic Connection Methods II

$$E_{xc} = \int_0^1 \left\langle \Psi(\lambda) \middle| V_{xc} \middle| \Psi(\lambda) \right\rangle d\lambda \quad (30)$$

- Non-interacting limit: only component of **V** is exchange (from antisymmetry of the wf).
- Slater determinant of the KS orbitals *is* the exact wave function for the non-interacting Hamiltonian operator.
- Expectation value: exact exchange for the non-interacting system. Compute as in a HF calculation. Use KS orbitals.
- Area of the rectangle defined by integration in next slide is thus E_x^{HF}

Adiabatic Connection Methods III

$$E_{xc} = \int_0^1 \langle \Psi(\lambda) | V_{xc} | \Psi(\lambda) \rangle d\lambda$$



$(1, < \Psi(1)\ |\ \mathbf{V}_{xc}\ |\ \Psi(1) >)$

$(0, < \Psi(0)\ |\ \mathbf{K}\ |\ \Psi(0) >)$

Area that we **want**

Area = exact *exchange-correlation energy*

$(1, < \Psi(0)\ |\ \mathbf{K}\ |\ \Psi(0) >)$

Area = HF exchange energy

Adiabatic Connection IV

- Area that we want: fraction *z* of the area of the rectangle above, which itself has area

$$\left\langle \Psi(1) \middle| V_{xc}(1) \middle| \Psi(1) \right\rangle - E_x^{HF} \quad (31)$$

- We do not know z. Consider it as an empirical parameter to be optimized.
- Approximate the right endpoint with E_{xc} computed with some choice of DFT, so area of top rectangle is E_{xc}^{DFT}
- Total area under the curve.

$$E_{xc} = E_x^{HF} + z\left(E_{xc}^{DFT} - E_x^{HF}\right) \quad (32)$$

Adiabatic Connection V

$$E_{xc} = E_x^{HF} + z\left(E_{xc}^{DFT} - E_x^{HF}\right) \quad (32)$$

- In practice (32) is written using another variable $a = 1 – z$

$$E_{xc} = (1-a)E_{xc}^{DFT} + aE_x^{HF} \quad (33)$$

- Analysis forms the basis of the ‘adiabatic-connection method’ because it connects between the non-interacting and fully interacting states.

Adiabatic Connection VI

- If expectation value of the curve is a line, then *z* = 0.5: This defines the “Half and Half” method (H&H).
- Using LDA exchange-correlation, Becke (1993) showed that the H&H method has an error of 6.4 kcal/mol for enthalpy of formation of the G1 test set.
- Estimate *a* in a better way: perhaps include additional parameters if warranted.
- Becke (1993) developed a 3-parameter functional (B3).

$$E_{xc}^{B3PW91} = (1-a)E_x^{LSDA} + aE_x^{HF} + b\Delta E_x^{B} + E_c^{LSDA} + cE_c^{PW91} \qquad (34)$$

Adiabatic Connection VII

$$E_{xc}^{B3PW91} = (1-a)E_x^{LSDA} + aE_x^{HF} + b\Delta E_x^{B} + E_c^{LSDA} + cE_c^{PW91} \qquad (34)$$

- Where a,b,c were optimized to 0.20, 0.72, 0.81.
- The name B3PW91: three-parameter scheme, GGA exchange, correlation functionals B and PW91.
- Model modified to use LYP instead of PW91 by Stephens et al. LYP is designed to compute the full correlation energy and not a correction to LSDA

Adiabatic Connection VIII

- B3LYP model is defined as

$$E_{xc}^{B3LYP} = (1-a)E_x^{LSDA} + aE_x^{HF} + b\Delta E_x^{B} + (1-c)E_c^{LSDA} + cE_c^{LYP} \quad (35)$$

- *a,b,c* same values as in B3PW91.
- Of all the modern functionals B3LYP has proven the most popular to date, although its reign seems to be ending.
- Adiabatic Connection methods incorporate both HF and DFT: hybrid methods (including HF means N^4 scaling).

Mix GGA with Hartree-Fock exchange.

Kohn-Sham theory (1965) – equation for orbitals:

$$\left(T + V_{\text{ne}} + V_{\text{ee}} + \boxed{\frac{\partial F_{\text{x}}}{\partial \rho}} + \frac{\partial F_{\text{c}}}{\partial \rho}\right)\varphi_i = \varepsilon_i \varphi_i$$

Compare Hartree-Fock theory (1930):

$$\left(T + V_{\text{ne}} + V_{\text{ee}} + \boxed{V_{\text{x}}^{\text{HF}}}\right)\varphi_i = \varepsilon_i \varphi_i$$

Advantages: Attractive HF exchange cancels self-interaction in V_{ee}

Hybrid DFT (Becke 1993):

$$\left(T + V_{\text{ne}} + V_{\text{ee}} + \boxed{\frac{X}{100} V_{\text{x}}^{\text{HF}} + \left(1 - \frac{X}{100}\right)\frac{\partial F_{\text{x}}}{\partial \rho}} + \frac{\partial F_{\text{c}}}{\partial \rho}\right)\varphi_i = \varepsilon_i \varphi_i$$

(*39,000+ citations in March 2013*)

Hybrid DFT was a breakthrough.

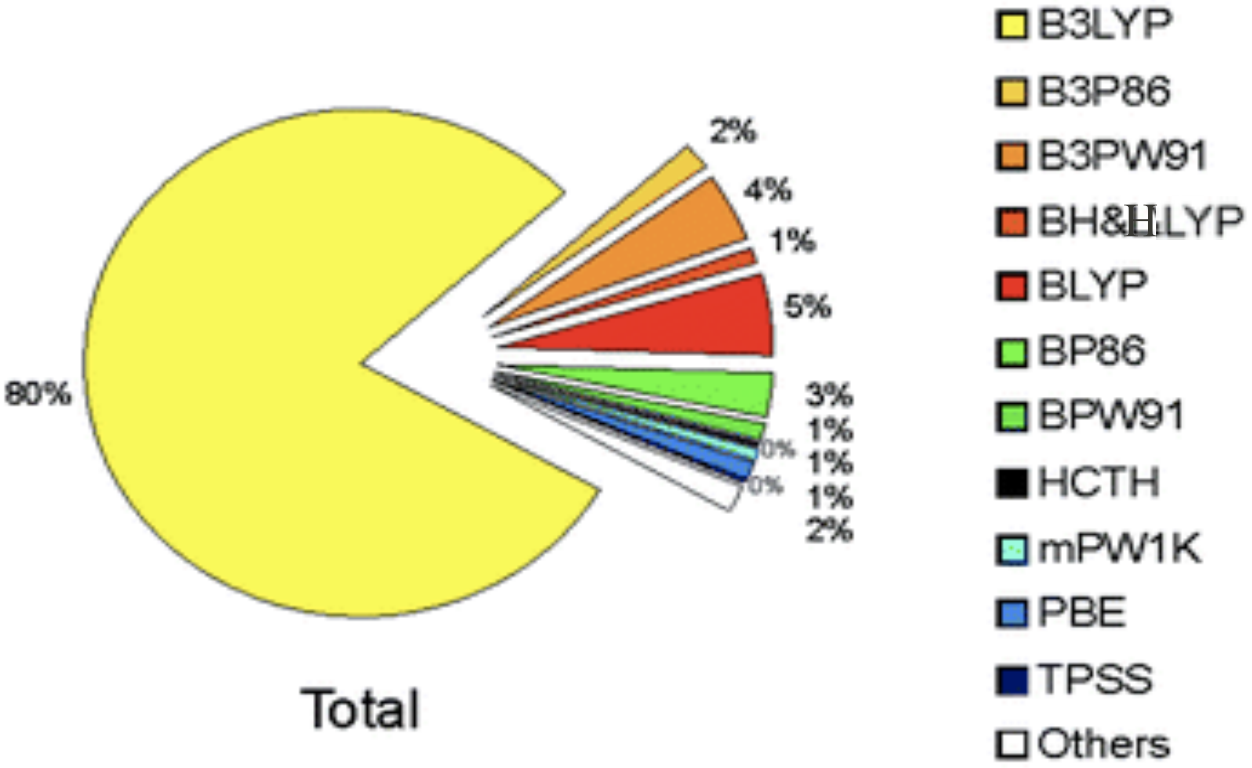
	Mean (unsigned) errors in kcal/mol	
	Bond energies	Barrier heights
Hartree-Fock theory	31	9
Local spin-density approximation	16	18
Correct thru 2nd order: SOGGA	7	13
GGA: BLYP (1988)	1.5	8
Hybrid: B3LYP (1993)	0.9	4

Becke–3 parameter–Lee-Yang-Parr

“chemical accuracy” for main-group bond energies, bond lengths, ...

This was the tipping point—making DFT the accepted everyday tool.

B3LYP is enormously popular.



Sousa, Fernandes, Ramos, *JPC A* (2007)

Density Functional Theory

Wrap-up

Video V.viii

DFT versus MO theory

- DFT optimizes an electron density while WFT theory optimizes a wave function.
- To determine a molecular property:
- In DFT: how does the property depend on the density?
- In MO theory: need to know the quantum mechanical operator.
- WF has a broader utility because there are more well-characterized operators than there are generic property functionals of the density.
- Example: total energy of interelectronic repulsion:
- Even if we had the exact density, exact exchange-correlation energy functional not known: exact interelectronic repulsion cannot be computed.
- With the exact wave function, evaluate the expectation value for the interelectronic repulsion operator

$$E_{ee} = \left\langle \Psi \middle| \sum_{i<j} \frac{1}{r_{ij}} \middle| \Psi \right\rangle \quad (36)$$

DFT versus MO theory II

- There is a DFT wave function. How useful is it?
- Slater Determinant from the KS orbitals is the exact wave function for the fictional non-interacting system having the same density as the real system.
- Properties of the KS determinants: extremely low level of spin contamination, even for cases where HF behaves badly.
- It is by no means guaranteed that the expectation value for S^2 over the KS determinant has any relationship at all to the corresponding expectation value over the exact wave function that corresponds to the KS density.
- Empirical observation suggests that DFT is more robust in dealing with open-shell systems where HF shows high spin contamination.
- In WFT methods, excited states can be generated as linear combinations of determinants derived from exciting one or more electrons from occupied to virtual orbitals.
- DFT applied to excited states requires invocation of time-dependent formalism.

Computational Efficiency I

- Scaling of local DFT no worse than N^3.
- For programs that use approximately the same routines and algorithms to perform a HF and DFT calculation, the cost of DFT is ca. double that of HF (15 atoms), but scaling gives DFT the win very quickly thereafter.
- Improvement using basis functions which are not contracted Gaussians.
- A density can be represented using an auxiliary basis set or numerically.
- Slater-type functions can be used.

Computational Efficiency II

- Plane waves as basis sets in periodic infinite systems.
- Large number of plane waves to represent the aperiodic densities that are possible within the unit cells, the necessary integrals are simple to solve.
- Used in dynamics and solid-state physics.
- Convergence with respect to basis set is typically much more rapid in DFT than in WFT methods.
- Linear scaling DFT available.
- Most of above optimal with *local* DFT functionals.

Limitations of KS

- Most applications in DFT are run within the KS formalism.
- It permits the kinetic energy to be computed as the expectation value of the kinetic-energy operator over the KS single determinant.
- No need to determine the kinetic energy as a functional of the density.
- Some systems not well described by a single Slater determinant.
- Need to introduce non-dynamical correlation but not double count.

Systematic Improvability

- WF theory: well defined path to the exact solution (Full CI with infinite basis).
- In DFT, how to do a better calculation?
- All current functionals are approximate for molecular systems.
- No obvious way to determine which functional may be optimal for a particular case.
- Basis set convergence can be explored.
- Compare behavior of different functionals.
- Compare with a highly correlated MO treatment.
- Compare with experiment.
- Experience shows that for a large variety of systems DFT is quite robust.

Older popular functionals have deficiencies:

#1

No functional prior to 2005 is “good” for both barrier heights
and transition metal bond energies.

The best functionals for organic chemistry are bad
for transition metal bond energies and vice versa.

#2

Most functionals prior to 2005 are bad for barrier heights
and noncovalent interactions, especially π-π stacking.

#3

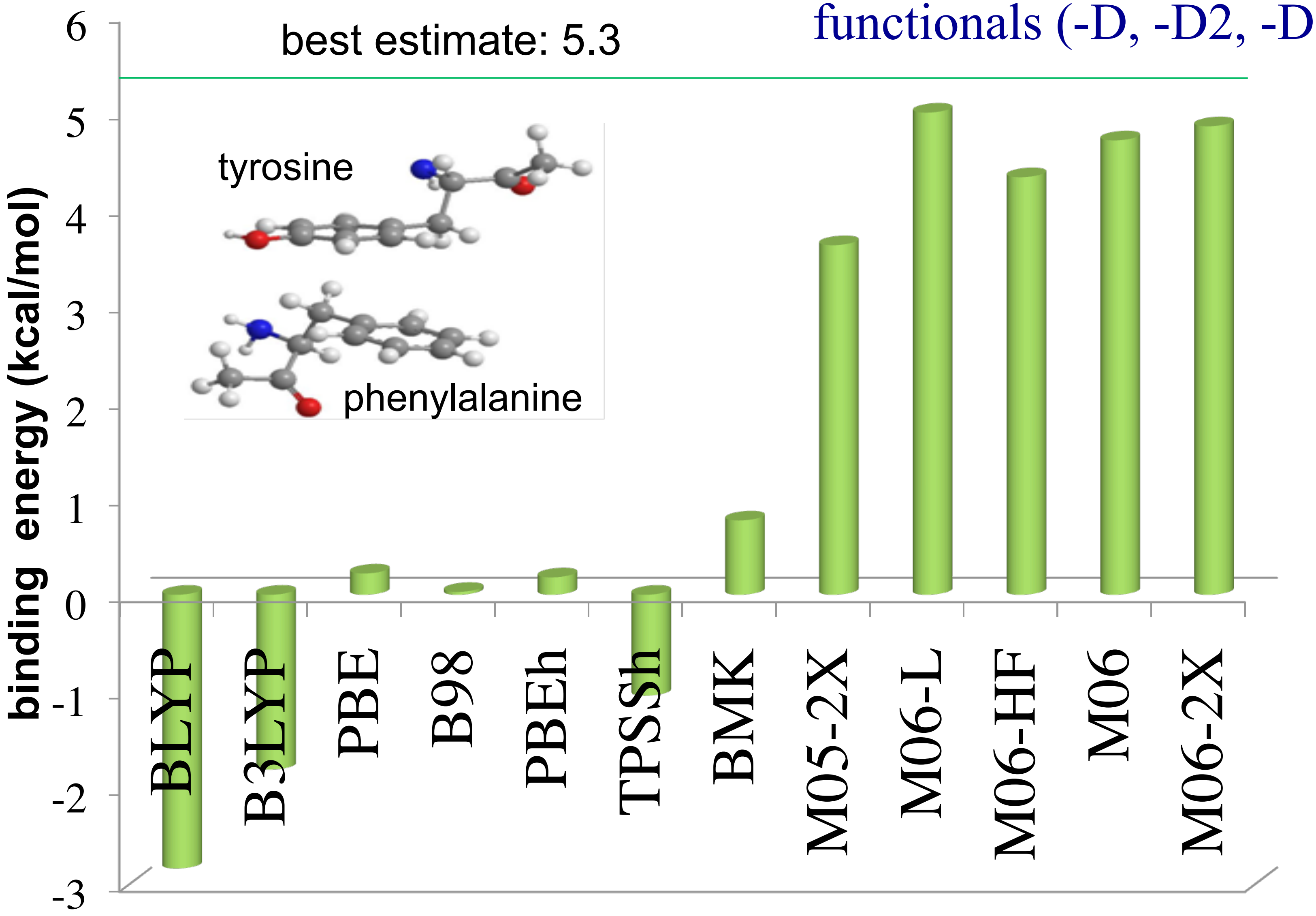
Standard functionals are *terrible* for charge-transfer excitations.

#4 (a practical issue)

DFT with Hartree-Fock exchange is too
expensive for many applications.

Amino acid residue pair with both electrostatics and π···π stacking

Molecular-mechanics-like add-on dispersion terms (protocols) have been developed for older functionals (-D, -D2, -D3)



Can (?) a functional do well for all 4 of:

Bond energies (main group)
Barriers (main group)
Noncovalent (S22)
TM: transition metal bond and reaction energies

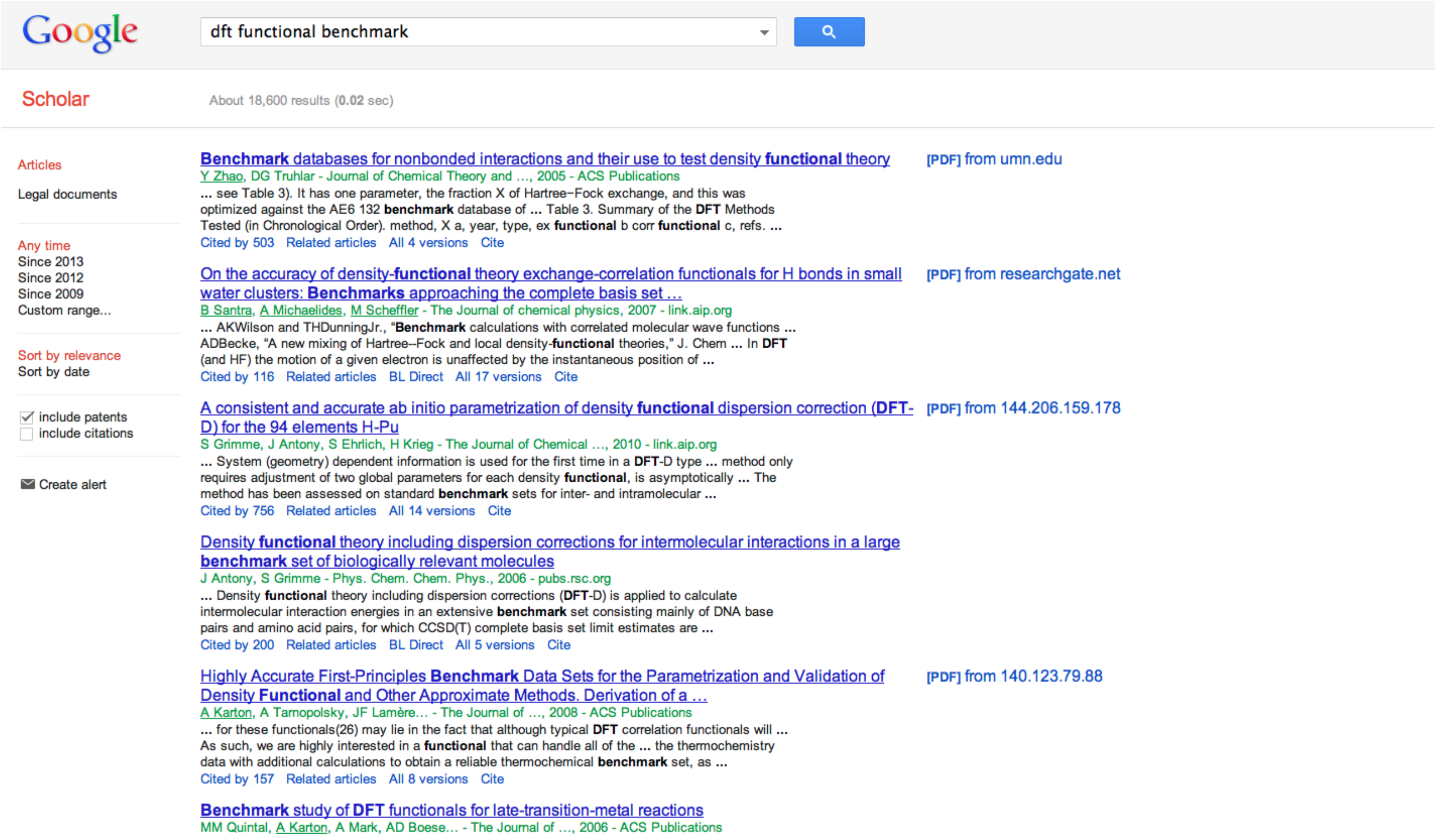
Mean error in kcal		*X*	bonds	barriers	noncov.	TM
best hybrid GGA for main group	B97-3	~27	0.6	2	4	17
popular hybrid GGA	B3LYP	20	0.9	4	4	12
new hybrid meta	**M06**	**27**	**0.6**	**2**	**0.8**	**6**

Significant savings are provided by working without HF exchange.

Example: $C_{104}H_{30}N_4$ local 17 hours
nonlocal 250 hours

"best" local	VS98	0	0.6	5	7	9
	TPSS	0	1.0	8	3	8
new local	**M06-L**	**0**	**0.8**	**4**	**0.8**	**6**

And Today?



dft functional benchmark

About 18,600 results (**0.02** sec)

[**Benchmark** databases for nonbonded interactions and their use to test density **functional** theory](#) [PDF] from umn.edu
Y Zhao, DG Truhlar - Journal of Chemical Theory and …, 2005 - ACS Publications
... see Table 3). It has one parameter, the fraction X of Hartree−Fock exchange, and this was optimized against the AE6 132 **benchmark** database of ... Table 3. Summary of the **DFT** Methods Tested (in Chronological Order). method, X a, year, type, ex **functional** b corr **functional** c, refs. ...
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[On the accuracy of density-**functional** theory exchange-correlation functionals for H bonds in small water clusters: **Benchmarks** approaching the complete basis set …](#) [PDF] from researchgate.net
B Santra, A Michaelides, M Scheffler - The Journal of chemical physics, 2007 - link.aip.org
... AKWilson and THDunningJr., "**Benchmark** calculations with correlated molecular wave functions ... ADBecke, "A new mixing of Hartree--Fock and local density-**functional** theories," J. Chem ... In **DFT** (and HF) the motion of a given electron is unaffected by the instantaneous position of ...
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[A consistent and accurate ab initio parametrization of density **functional** dispersion correction (**DFT**-D) for the 94 elements H-Pu](#) [PDF] from 144.206.159.178
S Grimme, J Antony, S Ehrlich, H Krieg - The Journal of Chemical …, 2010 - link.aip.org
... System (geometry) dependent information is used for the first time in a **DFT**-D type ... method only requires adjustment of two global parameters for each density **functional**, is asymptotically ... The method has been assessed on standard **benchmark** sets for inter- and intramolecular ...
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[Density **functional** theory including dispersion corrections for intermolecular interactions in a large **benchmark** set of biologically relevant molecules](#)
J Antony, S Grimme - Phys. Chem. Chem. Phys., 2006 - pubs.rsc.org
... Density **functional** theory including dispersion corrections (**DFT**-D) is applied to calculate intermolecular interaction energies in an extensive **benchmark** set consisting mainly of DNA base pairs and amino acid pairs, for which CCSD(T) complete basis set limit estimates are ...
Cited by 200 Related articles BL Direct All 5 versions Cite

[Highly Accurate First-Principles **Benchmark** Data Sets for the Parametrization and Validation of Density **Functional** and Other Approximate Methods. Derivation of a …](#) [PDF] from 140.123.79.88
A Karton, A Tarnopolsky, JF Lamère… - The Journal of …, 2008 - ACS Publications
... for these functionals(26) may lie in the fact that although typical **DFT** correlation functionals will ... As such, we are highly interested in a **functional** that can handle all of the ... the thermochemistry data with additional calculations to obtain a reliable thermochemical **benchmark** set, as ...
Cited by 157 Related articles All 8 versions Cite

[**Benchmark** study of **DFT** functionals for late-transition-metal reactions](#)
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