

Lecture 3: Density Functional Theory (DFT): applications and performance

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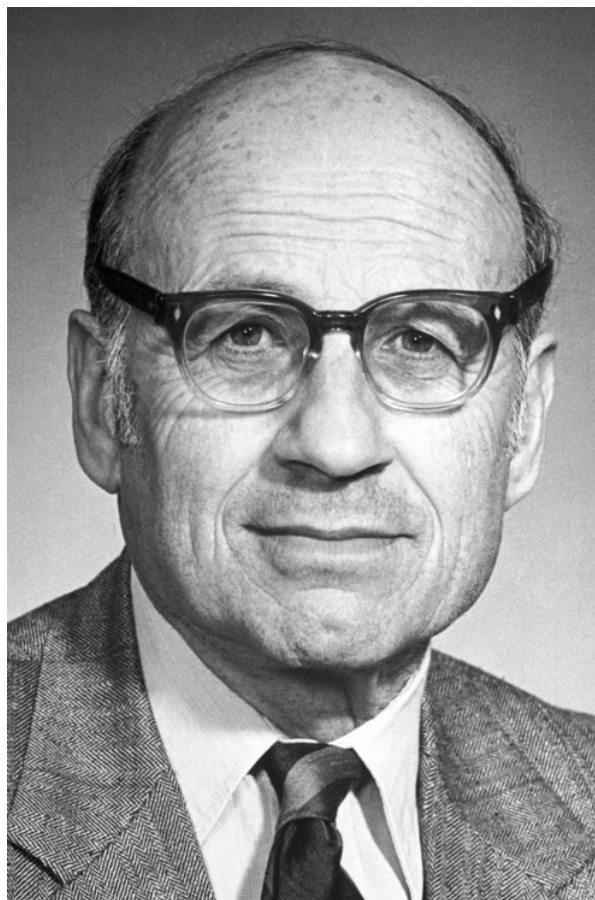
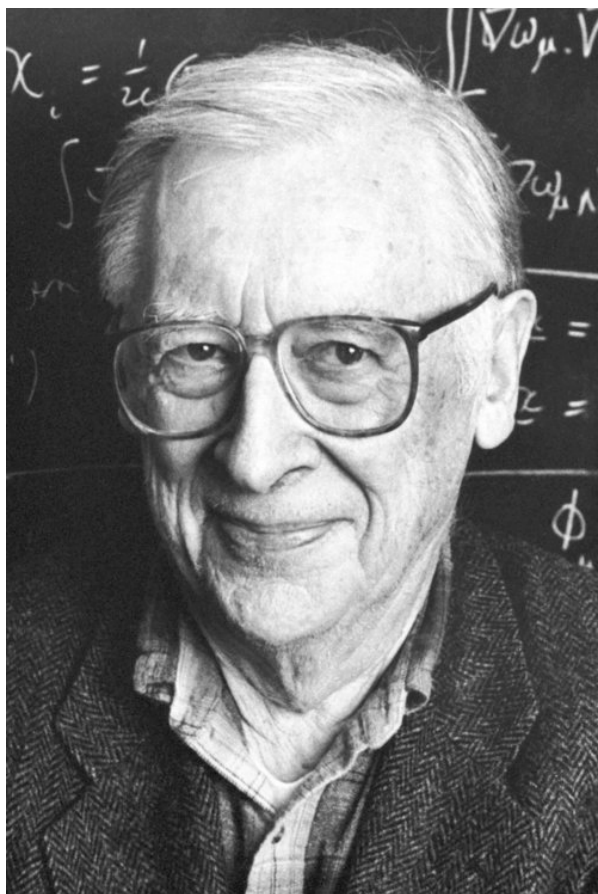
Sergey Levchenko (lecturer)

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Guest Lecturers (e.g. use of Abinit, FHI-aims, USPEX)

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The Computational Chemistry Nobel Prize



Walter Kohn

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry."

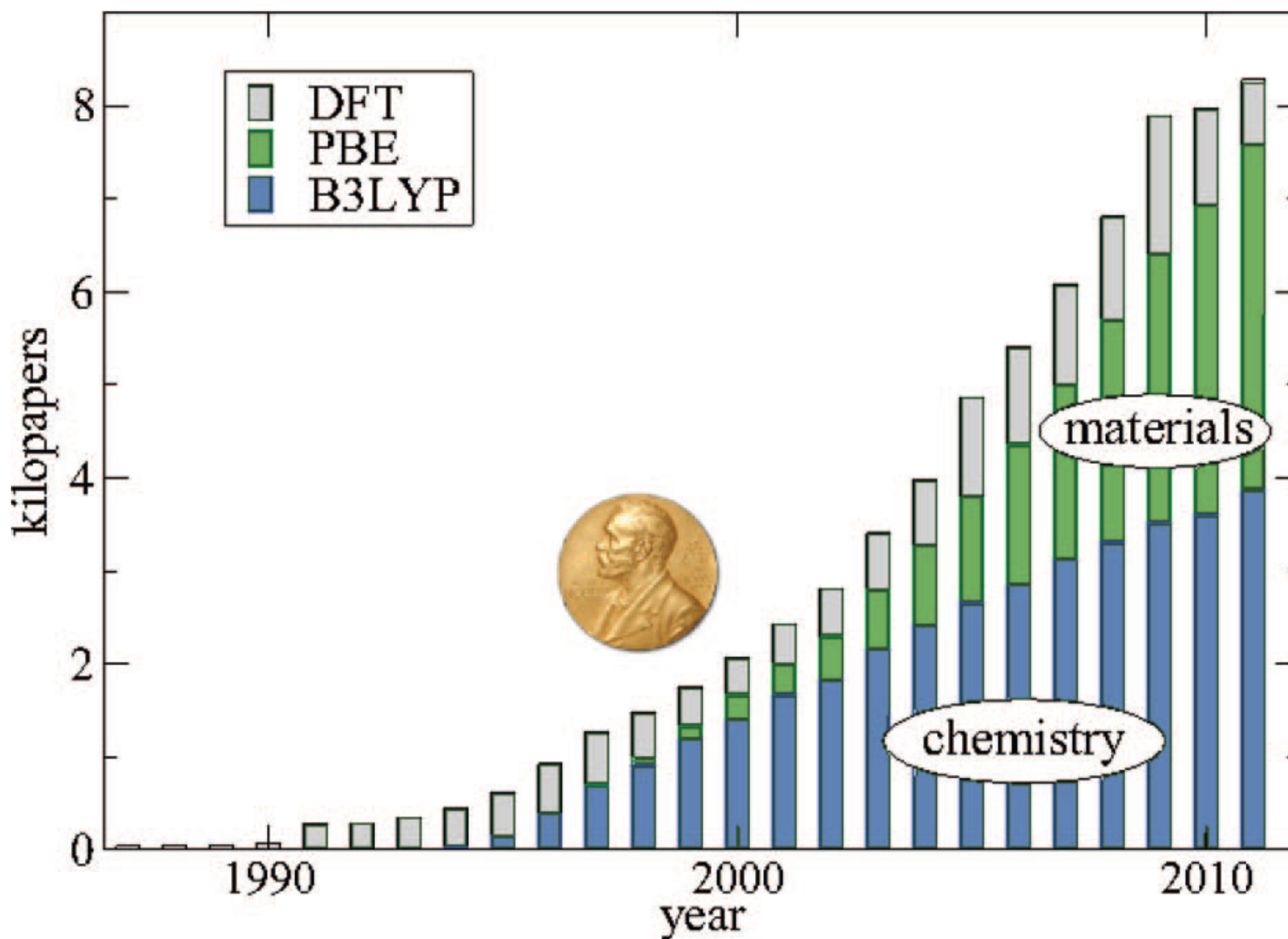
Outline

- Strengths and limitations of wavefunction approaches
- Introduction of density functional concept
- The Hohenberg–Kohn theorems for DFT
- Kohn-Sham system, practical solution
- LDA, GGA and hybrid functionals: construction and application scope
- Practical considerations for DFT simulations

Perspective on density functional theory

Kieron Burke

THE JOURNAL OF CHEMICAL PHYSICS 136, 150901 (2012)



21 kPapers
for 2020
and
counting

The Electronic Structure Problem

- A molecule composed from nuclei and electrons bound by Coulomb interactions
- Separate electronic (fast) from nuclei (slow) motion (adiabatic or Born-Oppenheimer approximation)
- Assign finite basis size (lattice) – Gaussian (Gaussian, Turbomole, Q-Chem, etc.) or plain waves (VASP, etc.) or Slater (ADF, etc.)
- Solve the Schrodinger equation for molecular electronic Hamiltonian:

$$\left[-\frac{1}{2} \sum_i \nabla_i^2 - \sum_{iA} \frac{Z_A}{r_{iA}} + \sum_{i>j} \frac{1}{r_{ij}} \right] \psi_e(\mathbf{r}; \mathbf{R}) = E_e \psi_e(\mathbf{r}; \mathbf{R})$$

Method	Hamiltonian	Wavefunction	Cost
Ab initio (e.g. HF, CAS-CI, CC-EOM)	Exact	Approximate (All electronic correlations)	Large (~10 atoms)
Density Functional (e.g. DFT, TDDFT)	Approximate, $F(\rho)$, (All electronic correlations)	Fixed (Kohn-Sham system, mean field)	Significant (~100 atoms)
Semiempirical (e.g. AM1, MNDO, INDO/S)	Approximate, (Some electronic correlations)	Approximate (Some electronic correlations)	Low (~1000 atoms)
Tight-binding (e.g. Huckel, Frenkel, SSH)	Approximate, (Min electronic correlations)	Approximate (Usually uncorrelated)	Low (~10,000 atoms)

Brief summary of post-HF methods

	CI	MP	CC
Size extensivity	no	yes	yes
Excited states	yes	no	yes
Ground state corrections beyond HF	yes	yes	yes
Ground state analytic gradients (low orders)	yes	yes	yes
Gaussian 09	QCISD,CAS	MP4	CCSD(T)
Firefly 8	yes	MP4	no
Q-Chem, Turbomole, GAMESS	yes	yes	yes

- *Accuracy: HF << MP2 < CISD < MP4(SDQ) ~ QCISD ~ CCSD < MP4 < CCSD(T)*
- *Reference state: HF ground state*
- *They work 'the best' when the reference HF state is accurate*
- *Shortcuts like restricting 'active space' are possible but use with caution*
- *Basis set complexity should increase concomitantly with method complexity*

Use them when you can afford their cost!
Systematic convergence to the exact answer

Problems with Wavefunction description of large systems

Let revisit computational expense:

2-electron system (e.g. H₂): 6-1=5 degrees of freedom $\Psi(r_1, r_2)$

p is the number of parameters per variable needed for the desired accuracy $3 < p < 10$.
Then we need $M = p^5 = 3^5 - 10^5 \approx 10^2 - 10^5$ parameters to describe the wavefunction.

Doable! Ab initio approaches work great for small molecules

For many electrons we are encountering an exponential wall

$$M = p^{3N}, \quad 3 \leq p \leq 10$$

“In general the many-electron wave function $\Psi(r_1, \dots, r_N)$ for a system of N electrons is not a legitimate scientific concept, when $N > N_0$, where $N_0 \sim 10^3$ ” (W. Kohn)

Hartree-Fock procedure – think density matrix!

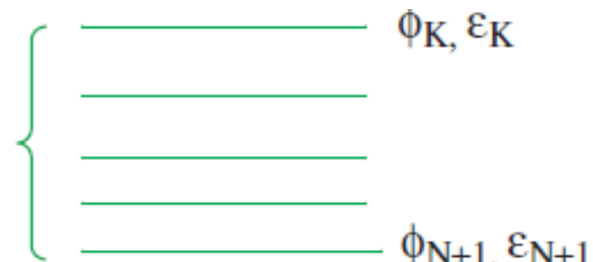
For simplicity, assume an even number of electrons (closed shell) and an orthogonal basis set

Looking for a solution of electronic problem,

$H_e \Psi = E \Psi$ where the wavefunction is a single Slater determinant $\Psi = |\phi_1 \dots \phi_N\rangle$ built on the (unknown) molecular orbitals

$$\phi_i(\mathbf{r}) = \sum_j^K C_{ij} \psi_j(\mathbf{r})$$

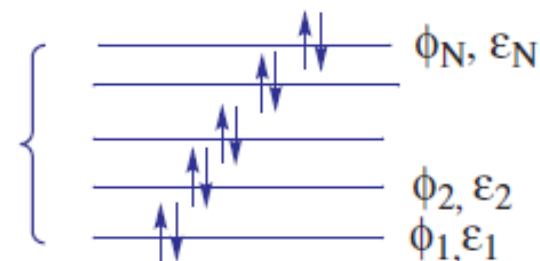
Virtual molecular orbitals



Ground state one-electron density matrix

$$\bar{\rho}_{nm} = 2 \sum_a^{occ} C_{na} C_{ma}^*$$

Occupied molecular orbitals



The Fock operator

$$F(\bar{\rho})_{nm} = t_{nm} + V(\bar{\rho})_{nm}$$

The Coulomb operator (V or G $\sim 2J-K$)

$$V(\bar{\rho})_{mn} = \sum_{k,l}^K \bar{\rho}_{kl} [\langle mk|nl\rangle - \frac{1}{2} \langle mn|kl\rangle]$$

The eigenvalue problem (secular equation)

$$FC = C\epsilon \quad \text{solves} \quad [F(\bar{\rho}), \bar{\rho}] = 0$$

Ground state energy $E = Tr(\bar{\rho}(F + t))$

The total energy $E + \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$

Nonlinear integro-differential equations, needs to be solved iteratively to achieve self-consistency!

Reduced description is needed!

Electronic density $\rho(r)$ for N-electron system $N = \int \rho(\mathbf{r}) d\mathbf{r}$ $\rho(\mathbf{r}) = N \langle \Psi | \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle$

$$\rho(\mathbf{r}_1) = N \underbrace{\int \int \cdots \int}_{N-1} |\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)|^2 \underbrace{d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_N}_{N-1}$$

Only for a single electron system: $\rho(\mathbf{r}) = \Psi^*(\mathbf{r})\Psi(\mathbf{r}) = |\Psi(\mathbf{r})|^2 = |\Psi\rangle \langle\Psi|$

Let define energy components for electronic Hamiltonian: $\hat{H}_e = \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$

Electron-nuclei interactions:

$$V_{\text{ne}}[\rho(\mathbf{r})] = \sum_k^{\text{nuclei}} \int \frac{Z_k}{|\mathbf{r} - \mathbf{r}_k|} \rho(\mathbf{r}) d\mathbf{r}$$

Electron-electron interactions:

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

Now we have a problem: what about $T(\rho(r))$?

Thomas-Fermi Functional (1927): $T_{\text{ueg}}[\rho(\mathbf{r})] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}$

Derived for a uniform electronic gas ('jellium'-like model) – read metals!

Did we forget something?

Pauli principle and exchange!

$$\left\langle \Psi \left| \sum_{i < j}^{\text{electrons}} \frac{1}{r_{ij}} \right| \Psi \right\rangle = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)h(\mathbf{r}_1; \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

The concept of a ‘hole function’ to correct for the energetic errors due to correlation and exchange (sometimes called ‘exchange-correlation hole’), i.e., exchange cannot be explicitly represented via ρ in a simple and analytical form!

Slater exchange-correlation form:
$$E_x[\rho(\mathbf{r})] = -\frac{9\alpha}{8} \left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}$$

(the exchange hole could be approximated as a sphere of constant potential with a radius depending on the magnitude of the density at that position)

So we constructed a first Density Functional (map density -> energy)

$$E[\rho(\mathbf{r})] = \frac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} + \sum_k^{\text{nuclei}} \int \frac{Z_k}{|\mathbf{r} - \mathbf{r}_k|} \rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 - \frac{9\alpha}{8} \left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}$$

The Hohenberg–Kohn Existence Theorem (1965)

The density as the basic variable: the external potential determines uniquely the charge density, and the charge density determines uniquely the external potential.

Or different formulation: Every observable of a stationary quantum mechanical system (including energy) can be calculated in principle exactly from the ground-state density alone, i.e. every observable can be written as a functional of the ground-state density.

Common sense: Within a Born-Oppenheimer approximation the ground state of the system of electrons is a result of positions of nuclei. Once the nuclei potential is in place everything else is, including electron density, which simply adjusts itself to give the lowest possible total energy of the system. The external potential is the only variable term in this equation and everything else depends indirectly on it. Is opposite true?

Proof: Let assume we have exact ground state density, non-degenerate ground state and existence of 2 distinct potentials (V_{ext} and V'_{ext}) that produce this ground state density (leading to 2 distinct Hamiltonians H and H' and wavefunctions Ψ and Ψ'): $E_0 = \langle \Psi | H | \Psi \rangle$ $E'_0 = \langle \Psi' | H' | \Psi' \rangle$

$$E_0 < \langle \Psi' | H | \Psi' \rangle = \overbrace{\langle \Psi' | H' | \Psi' \rangle} + \langle \Psi' | H - H' | \Psi' \rangle = E'_0 + \int \rho(\mathbf{r}) [\hat{V}_{ext} - \hat{V}'_{ext}] d\mathbf{r}$$

$$E'_0 < \langle \Psi | H' | \Psi \rangle = \underbrace{\langle \Psi | H | \Psi \rangle} + \langle \Psi | H' - H | \Psi \rangle = E_0 - \int \rho(\mathbf{r}) [\hat{V}_{ext} - \hat{V}'_{ext}] d\mathbf{r}$$

$$E_0 + E'_0 < E'_0 + E_0 \quad \textbf{Contradiction!}$$

The Hohenberg–Kohn Variational Theorem (1965)

The ground state density can be calculated in principle exactly using the variational method involving only density

For any trial $\tilde{\rho}(\mathbf{r})$ with $\tilde{\rho}(\mathbf{r}) \geq 0$ and $\int \tilde{\rho}(\mathbf{r}) d\mathbf{r} = N$ we have $E_0 \leq E[\tilde{\rho}]$

I.e., the first theorem indicates that this density determines a candidate wave function and Hamiltonian. That being the case, we can evaluate the energy expectation value

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

Optional reading: follow the discussion about N –representability of the density

So, in principle, we can keep choosing different densities and those that provide lower energies, however: no prescription how to get better densities and we cannot avoid dealing with the wavefunction.

A numerical self-consistent procedure for ‘improving’ the density in step-wise fashion is needed!

Euler-Lagrange equation

We can introduce a strict definition of the chemical potential!

$$\mu_i = \left(\frac{\partial U}{\partial N_i} \right)_{S, V, N_{j \neq i}}$$

So far HK2 theorem provided us with a path $\tilde{\rho} \rightarrow \hat{H}_{el} \rightarrow \tilde{\Psi}$; $\langle \tilde{\Psi} | H | \tilde{\Psi} \rangle = E[\tilde{\rho}] \geq E[\rho_0] \equiv E_0$

where $\rho_0(\mathbf{r})$ is the true ground state density of the real system

N-representability constrain: $constraint = \int \rho(\mathbf{r}) d\mathbf{r} - N = 0$

This means that we need to minimize a Lagrangian to get a variational solution:

$$E[\rho(\mathbf{r})] - \mu \left[\int \rho(\mathbf{r}) d\mathbf{r} - N \right] \quad \delta E[\rho(\mathbf{r})] - \mu \delta \left\{ \int \rho(\mathbf{r}) d\mathbf{r} \right\} = 0$$

Using: $\delta F = \int \frac{\delta F}{\delta f(x)} \delta f(x) dx$ We get: $\int \frac{\delta E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \delta \rho(\mathbf{r}) d\mathbf{r} - \mu \int \delta \rho(\mathbf{r}) d\mathbf{r} = 0$

This provides the condition for constrained minimization and defines the value of the Lagrange multiplier at minimum – a chemical potential

The chemical potential: $\mu = \frac{\delta E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}$

The Kohn-Sham system (1965)

The path $\tilde{\rho} \rightarrow \hat{H}_{el} \rightarrow \tilde{\Psi}$; $\langle \tilde{\Psi} | H | \tilde{\Psi} \rangle = E[\tilde{\rho}] \geq E[\rho_0] \equiv E_0$ is a dead end!

Kohn-Sham idea: let introduce a fictitious system of electrons (“the Kohn-Sham electrons”)

These electrons do not interact, and are subject to an external potential (the Kohn-Sham potential), such that their ground-state charge density and energy are IDENTICAL to the charge density and energy of the interacting system.

What is it good for? For a system of non-interacting electrons, the Slater determinant is the EXACT wavefunction. Moreover, the kinetic energy of the non-interacting system is well defined. WE HAVE AN ARTIFICIAL CONSTRUCT!

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

Non-interacting KS system

“The rest”

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

$$\rho = \sum_{i=1}^N \langle \chi_i | \chi_i \rangle - \text{Kohn-Sham single-electron orbitals (still cannot get rid of the wavefunction)}$$

Now we can go along the path for Kohn-Sham system, where the ‘unknown’ is in E_{xc}

Well, there could be a different opinion!

The Kohn-Sham equations

Now we have Hartree-Fock like system of equations!

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

$$h_i^{\text{KS}} = -\frac{1}{2} \nabla_i^2 - \sum_k^{\text{nuclei}} \frac{Z_k}{|\mathbf{r}_i - \mathbf{r}_k|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}} \quad V_{\text{xc}} = \frac{\delta E_{\text{xc}}}{\delta \rho}$$

Practical issues: we have a code that solves the HF problem, a lot of basis sets are programmed... why not to re-use those?

For practical purposes, modern computational software codes use the same AO basis sets and the matrix elements for the single-electron integrals (t_{ij}) and the two-electrons integrals $\langle ij|kl \rangle$ are usually the same in both *ab initio* and DFT computations.

$$F(\rho)_{nm} = t_{nm} + V(\rho)_{nm} + V_{nm}^{\text{xc}}(\rho) \quad V(\rho)_{mn} = \sum_{k,l}^K \rho_{kl} [\langle mk|nl \rangle - \frac{1}{2} c_x \langle mn|kl \rangle]$$

$$t_{nm} = \langle n | -\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|} | m \rangle \quad \langle nm|kl \rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_n^*(1) \psi_m^*(2) \frac{1}{r_{12}} \psi_k(1) \psi_l(2)$$

$$S_{nm} = \langle n|m \rangle \equiv \int d\mathbf{r}_1 \psi_n^*(1) \psi_m(1) \quad \text{Note: } c_x=1, V_{\text{xc}}=0 \rightarrow \text{HF limit; } c_x=0 \rightarrow \text{pure DFT limit!}$$

Exactly the same eigenproblem

$$\underline{FC = SC\varepsilon}$$

But what is $V_{\text{xc}}?????$ $V_{\text{xc}} = \frac{\delta E_{\text{xc}}}{\delta \rho}$

What is the difference between HF and DFT?

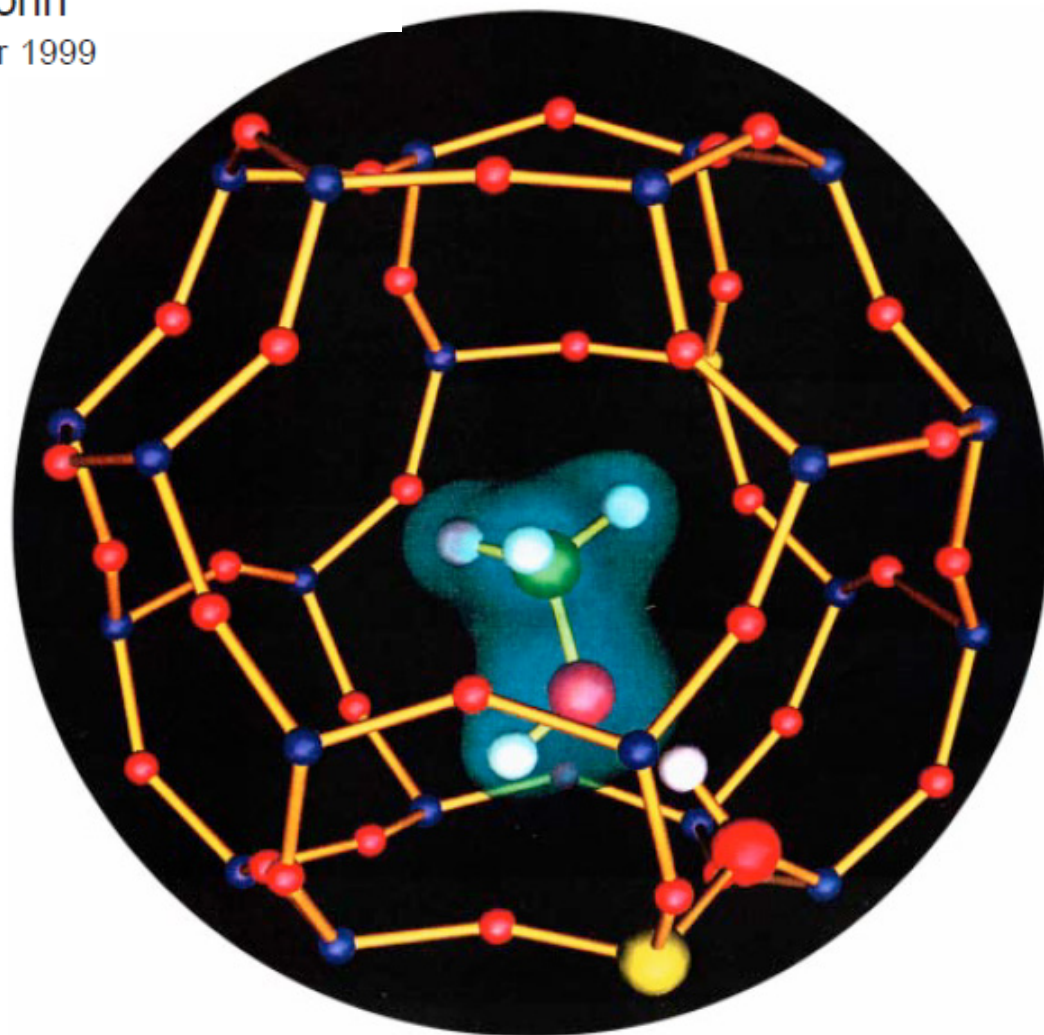
- DFT contains no approximations: it is formally *exact*. All we need to know is E_{xc} as a function of ρ
- HF is a deliberately *approximate* theory, whose development was in part motivated by an ability to solve the relevant equations *exactly* given the appropriate form of the wavefunction (i.e. Slater determinant)
- While DFT is an *exact* theory, but the relevant equations must be solved *approximately* because a key operator $E_{xc}(\rho)$ has unknown form.

Case study 1: DFT successes

Nobel Lecture: Electronic structure of matter—wave functions and density functionals*
W. Kohn

Reviews of Modern Physics, Vol. 71, No. 5, October 1999

FIG. 1. Methanol inside a cage of the zeolite sodalite. Zeolites are crystalline arrays of cages built of silicon (blue), aluminum (yellow), and oxygen (red) atoms. For each Al atom one must have a positive counter ion [in this case H^+ (white)]. A methanol molecule is inside the cage (carbon is green) where it can react with the proton. DFT calculations have assigned and clarified the IR spectra, have determined the binding sites of methanol, and have calculated the activation energy for the reaction. Acid catalysis in zeolites is widely used in the chemical industry (after E. Nusterer, P. Bloechl, and K. Schwarz, 1996, *Angew. Chem.* **35**, 175).

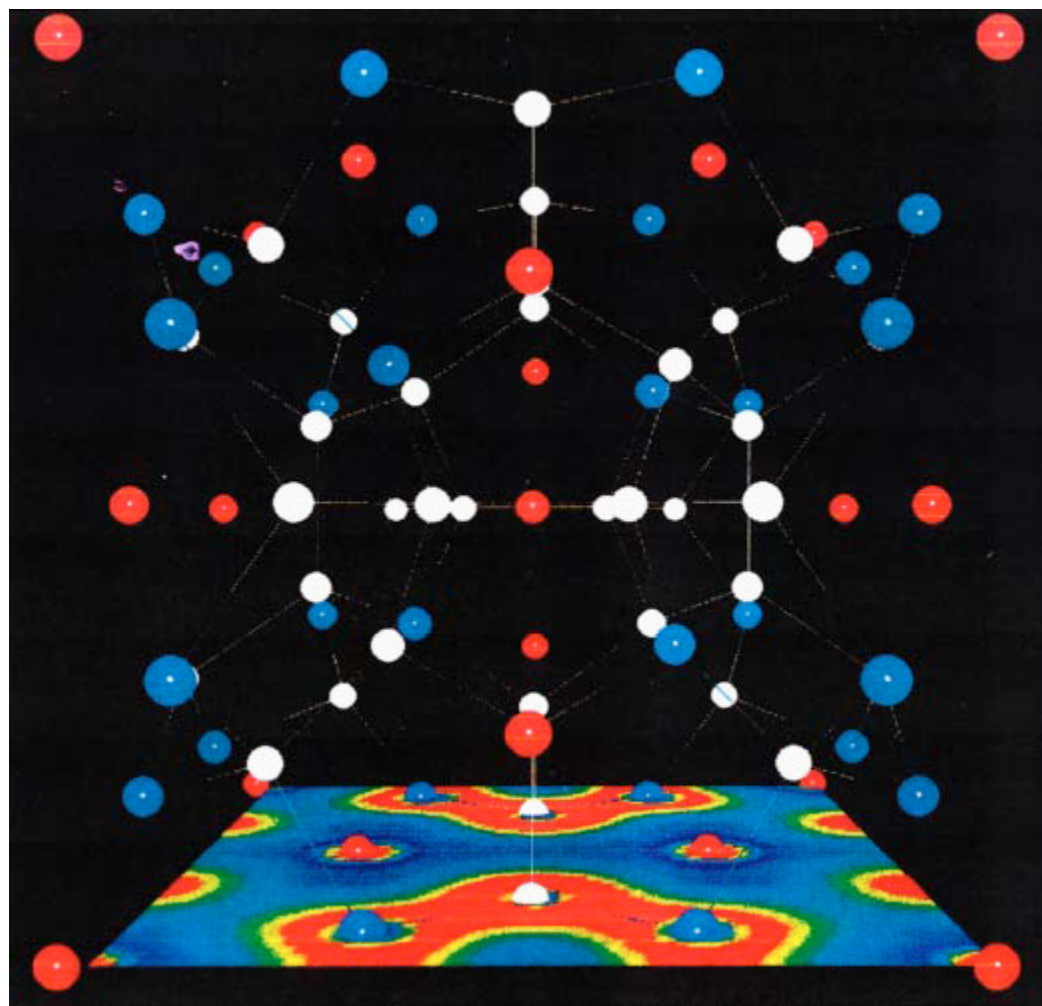


Case study 1: DFT successes

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FIG. 2. The geometric structure of the clathrate $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ (Sr, red; Ga, blue; Ge, white) and its charge density in a plane bisecting the centers of the cages. DFT calculations have shown that the Sr atoms are weakly bound and scatter phonons effectively, thereby lowering thermal conductivity. However, contrary to intuitive expectations, the Sr atoms do not donate electrons to the frame and are practically neutral. Conductivity is due to electrons traveling through the frame, not through the one-dimensional Sr “wires” in the structure; there is thus little scattering of conduction electrons by Sr vibrations. For these reasons, the compound is a metal. (theory by N. P. Blake and H. Metiu, submitted for publication)

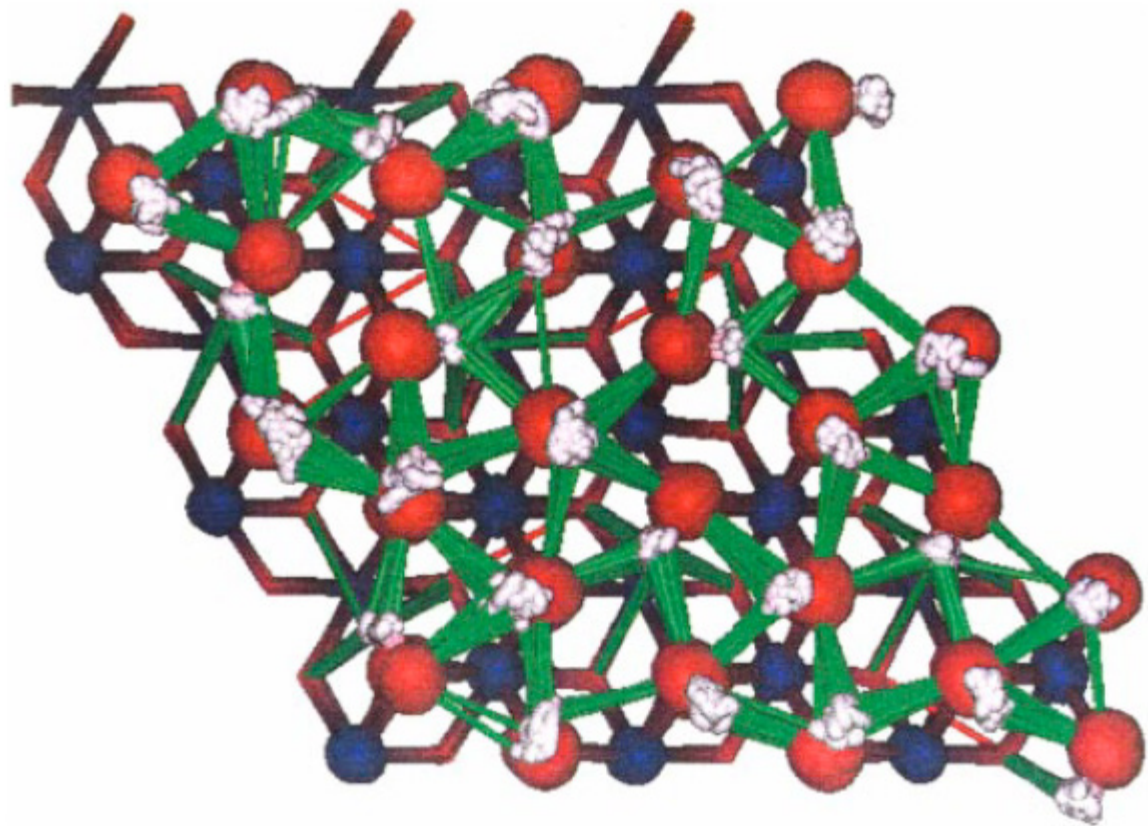


Case study 1: DFT successes

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FIG. 3. Fully hydroxylated aluminum (0001) surface (red, O; blue, interior Al; Al; gray, H atoms; the green lines are H bonds). Each surface Al atom in Al_2O_3 has been replaced by three H atoms. The figure represents a superposition of configurations in a molecular-dynamics simulation at regular intervals of 1 ps. These calculations help to understand the complex dynamics of water adsorption on aluminum [K. C. Haas *et al.*, *Science* **282**, 265 (1998)] [Color].



Discussion

1. What are the advantages and disadvantages of wavefunction methods?
2. What are the advantages and disadvantages of DFT methods?
3. Question to all: write on the chat what is exchange-correlation hole function in a system of 1 electron?

Step 1: Local Density Approximation (LDA) – we can describe metals!

LDA is the simplest and the often only an explicit component of many functionals.

$$E_{xc}^{\text{LDA}}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho) d\mathbf{r}, \quad E_{xc} = E_x + E_c,$$

Homogeneous electron gas (interacting electrons into a volume, V , with a positive background charge keeping the system neutral).

Slater-like exchange form:

$$E_x^{\text{LDA}}[\rho] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int \rho(\mathbf{r})^{4/3} d\mathbf{r}.$$

Correlation functional is not exact $\epsilon_c = A \ln(r_s) + B + r_s(C \ln(r_s) + D)$, High density

$$\epsilon_c = \frac{1}{2} \left(\frac{g_0}{r_s} + \frac{g_1}{r_s^{3/2}} + \dots \right), \text{ Low density} \quad \frac{4}{3} \pi r_s^3 = \frac{1}{\rho}. \quad (\text{Wigner-Seitz radius})$$

Finally we have

$$v_{xc}^{\text{LDA}}(\mathbf{r}) = \frac{\delta E^{\text{LDA}}}{\delta \rho(\mathbf{r})} = \epsilon_{xc}(\rho(\mathbf{r})) + \rho(\mathbf{r}) \frac{\partial \epsilon_{xc}(\rho(\mathbf{r}))}{\partial \rho(\mathbf{r})}.$$

Notation LSDA refers to the ability to describe spin state by separating up and down spin comp.

Bottom line: if you need to describe metals, look no further! LDA/LSDA

Note: long-range exchange is completely screened!

Step 2: Generalized Gradient Approximation (GGA) – on the way to inhomogeneous density in molecules!

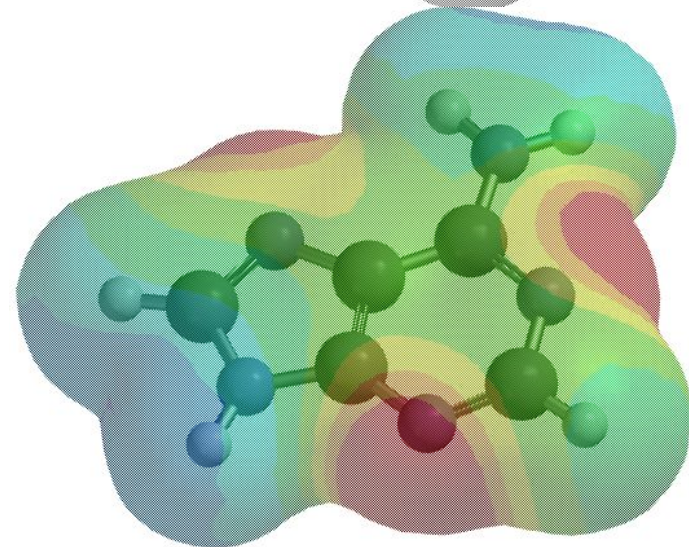
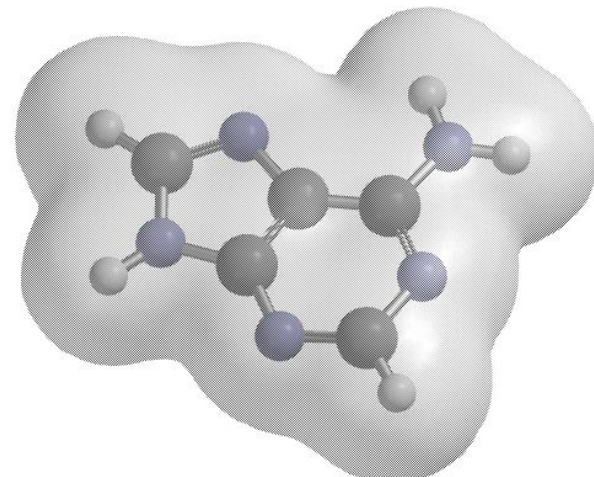
Compared to metals, in a molecular system, the electron density is NOT spatially uniform.

GGA functionals are still local but also take into account the gradient of the density at the same coordinate. Sometimes GGA is labeled as ‘semi-local’. GGA is typically preserving analytical – scaling – features of the unknown exact xc functional

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

GGA provides very good results for molecular geometries and ground-state energies!

Bottom line: optimization of molecular geometries (ground state structure and conformers), chemical energies – look no further (BLYP, PBE, BP87)



Step 3: Hybrid DFT – standing in between insulators and metals

Add a fraction (c_x or a) of Hartree-Fock exchange to the functional (i.e. ‘screened’ exchange)

$$E_{xc} = (1 - a)E_{xc}^{\text{DFT}} + aE_x^{\text{HF}} \quad V(\rho)_{mn} = \sum_{k,l}^K \rho_{kl} [\langle mk|nl \rangle - \frac{1}{2}c_x \langle mn|kl \rangle]$$

Hybrid functionals are ‘non-local’. Inclusion of HF exchange in a hybrid functional makes up for an underestimation by pure functionals of the importance of ionic terms in describing polar bonds. GGA functionals have certain systematic errors (e.g., underestimate barrier heights in chemical reactions). Hartree–Fock theory has frequently opposite trends. Hybrids stand in the middle.... Interplay between metal (LDA) and insulator (HF) character.

Most popular functional ever: B3LYP (Becke, three-parameter, Lee-Yang-Parr)

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

Becke's fitting to a set of atomization energies, ionization potentials, proton affinities, and total atomic energies. **THE DAWN OF SEMIEMPIRICAL DFT**

Bottom line: very good for optimization of molecular geometries (ground state structure and conformers), chemical energies, reasonable band-gap, good starting point for TDDFT – look no further (B3LYP(20%HF), PBE1PBE(25%HF), BHandHLYP(50%HF))

Step 4: Other DFT developments

First principle functionals

- Meta-GGA (e.g. TPSS), dependence on $\rho, \nabla\rho, \nabla^2\rho$
- Hyper-GGA (e.g. TPSSh), dependence on $\rho, \nabla\rho, \nabla^2\rho$ *HF exchange*
- Generalized RPA (e.g., OEP2), dependence on $\rho, \nabla\rho, \nabla^2\rho$ *HF exchange Virtual orbitals*

Semiempirical functionals

- Range corrected (e.g. CAM-B3LYP, LC-wPBE, LC-BLYP, wB97xD): restore ~100% of exchange at long distances. Good for charged states, charge-transfer states, extended polarizable systems
- Short range hybrid (HSE): limit hybrid to a short range, so that periodic boundary conditions calculations are numerically amenable. Good for PBS where hybrids are important (e.g., metal-non-metal transition in condensed matter – Mott's transition).
- Dispersion corrected functionals (e.g. B97D3, wB97xD, PBE-MBD, vdW-DF2): include empirical dispersion schemes. Good when dispersive interactions are important (e.g. π - π stacking).
- Highly optimized functionals (e.g. Truhlar M0?? Family, like M06HF, M052X) – provide very accurate answers for very specific problems and molecular families they have been optimized for. Use with care, familiarize yourself with their purpose.
- DFTB: DFT-based semiempirical approach. Use for large systems and reduced numerical cost.

Bottom line: many good models are already available and more are showing up every day. Be cautious, get the right physics first, never 'go after the number' – you may get it for a wrong reason!

Range separated and IP-tuned functionals

Idea: one needs to restore the correct asymptotics at long ranges

$$v_{xc}(r) \sim -\frac{1}{r} + \Delta_{\infty}$$

The long-range corrected (LRC) functionals aim to fix this by separating short and long distance fraction of exchange

$$\omega_{\text{RSF}} = \text{erfc}(\gamma r_{12})$$

$$\omega_{\text{RSF}} = e^{(-\gamma r_{12})}$$

$$\frac{1}{r_{12}} = \underbrace{\frac{1 - [\alpha + \beta(1 - \omega_{\text{RSF}}(\gamma, r_{12}))]}{r_{12}}}_{\text{SR, DFT}} + \underbrace{\frac{\alpha + \beta(1 - \omega_{\text{RSF}}(\gamma, r_{12}))}{r_{12}}}_{\text{LR, HFT}}$$

Examples

$\alpha \neq 0$ $\beta = 0$ conventional global hybrids, e.g. B3LYP (20%)

$\alpha = 0$ $\beta \neq 0$ LC functionals, e.g. LC-PBE (0%/100%)

$\alpha \neq 0$ $\beta \neq 0$ CAM functionals, e.g. CAM-B3LYP (20%/65%)

Idea of IP tuning: one needs to restore the Koopman's theorem

$$\text{IP} = E_M - E_{M-1} = -\epsilon_{\text{HOMO}}$$

Example of IP-tuning for PBE functional:

the iterative procedure takes about 5-

10 cycles resulting in a UNIQUE

functional for each molecule

$$E_{xc}^{\text{PBEh},\alpha} = \alpha E_x^{\text{HF}} + (1 - \alpha) E_x^{\text{PBE}} + E_c^{\text{PBE}}$$

$$\Delta_{\text{IP}} = \left| -\epsilon_{\text{HOMO,neut}}^{\alpha} - (E_{\text{neut}}^{\alpha} - E_{\text{cat}}^{\alpha}) \right|$$

Bottom line: Range corrected and tuned functionals are needed when describing delocalized phenomena (delocalized charges, excitons, polarizabilities, etc.). Use them with caution based on physical arguments.

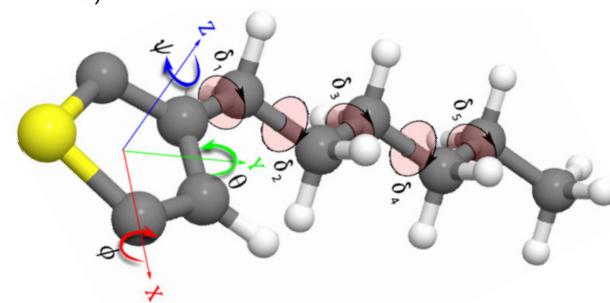
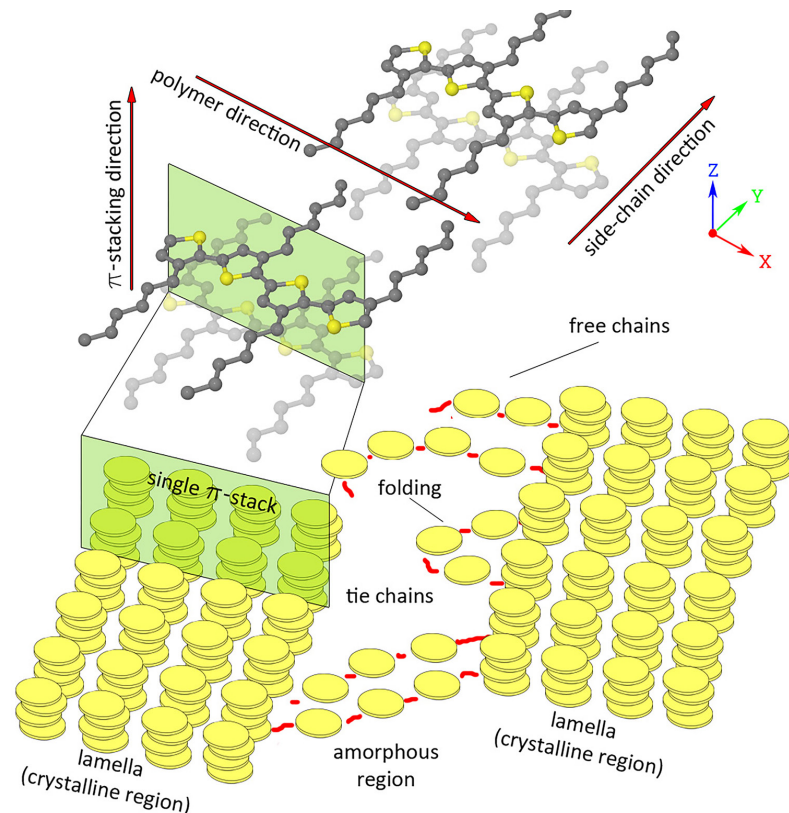
Case study 2: polymer chain packing

Table 1. Recently Reported Parameters of P3HT Unit Cell (in Chronological Order) Along with Relevant Results from the Present Work^a

method	polymer (Å)	π -stack (Å)	side-chain (Å)	angle (deg)
Interdigitated (Type-2) Structure				
ED, str. P3HT-26 ²⁰		9.3	13.1	68.5
X-ray ²¹		8.8	12.0	
this work (OPLS)	7.81	8.7	13.2	70.2
this work (PBE-MBD)	7.80	8.9	13.3	69.9
this work (vdW-DF2)	7.89	9.1	13.5	69.3

Table 2. Assessment of Density Functionals for P3HT Fragments: Polyethylene (PE), Polythiophene (PT), and P3HT Monomer (M)^a

	PE	PT	M
dataset size	6	7	72
Fixed Basis Set 6-311G*			
CAM-B3LYP-D3	5	9	5
B3LYP-D3	16	5	12
PBE-MBD	22	23	13
vdW-DF2	19	20	17
LC- ω PBE-D3	50	15	24
ω B97XD	90	16	26
OPLS	118	54	56
CAM-B3LYP	195	9	64



J. Phys. Chem. C 2018, 122, 9141–9151

Perdew Jacob's ladder to Heaven

Table 6.1 (from Jensen) Perdew classification of exchange–correlation functionals

Level	Name	Variables	Examples
1	Local density	ρ	LDA, LSDA, X_α
2	GGA	$\rho, \nabla\rho$	BLYP, OPTX, OLYP, PW86, PW91, PBE, HCTH
3	Meta-GGA	$\rho, \nabla\rho, \nabla^2\rho$ or τ	BR, B95, VSXC, PKZB, TPSS, τ -HCTH
4	Hyper-GGA	$\rho, \nabla\rho, \nabla^2\rho$ or τ <i>HF exchange</i>	H+H, ACM, B3LYP, B3PW91, O3LYP, PBE0, TPSSh, τ -HCTH-hybrid
5	Generalized RPA	$\rho, \nabla\rho, \nabla^2\rho$ or τ <i>HF exchange</i> <i>Virtual orbitals</i>	OEP2

Commonly used hybrid density functionals

Functional	ω, bohr^{-1}	$c_{\text{SR}}/c_{\text{LR}}$	X-DF(α_x)	C-DF(α_c)
B3LYP	—	0.2	B88(0.9)	LYP(0.81)
CAM-B3LYP	0.33	0.19 / 0.65	B88	LYP(0.81)
ω B97X	0.3	0.1577 / 1	B97'	B97
LC- ω PBE	0.4	0 / 1	PBE'	PBE
HSE06	0.11	0.25 / 0	PBE	PBE
M06-2X	—	0.54	M06-2X	M06-2X

$$E_{xc} = c_{\text{SR}} E_x^{\text{HF,SR}} + c_{\text{LR}} E_x^{\text{HF,LR}} + (1 - c_{\text{SR}}) E_x^{\text{DF,SR}} + (1 - c_{\text{LR}}) E_x^{\text{DF,LR}} + E_c^{\text{DF}}$$

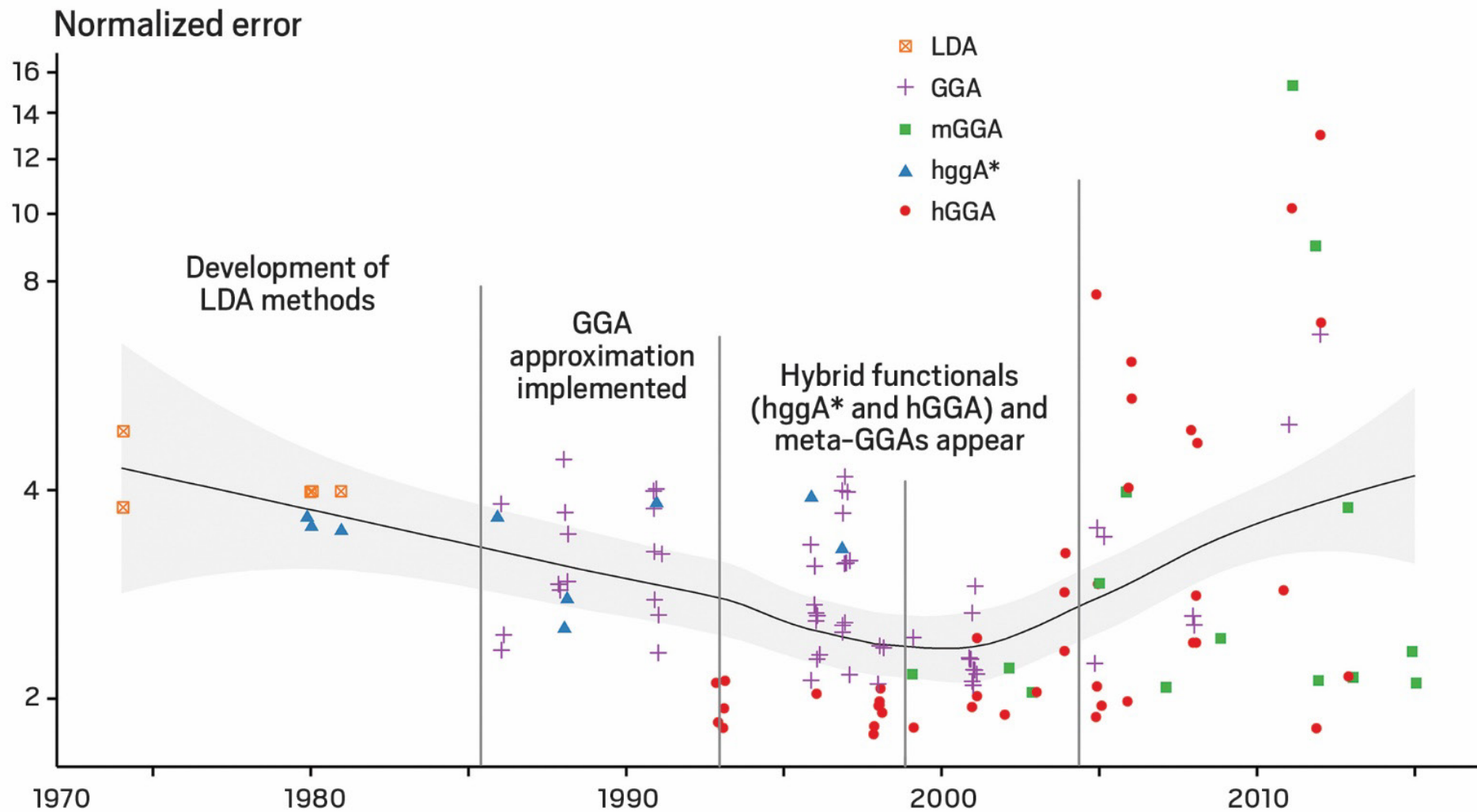
- $E_{x,c}^{\text{DF}} = E_{x,c}^{\text{DF,local}} + \alpha_{x,c} \Delta E_{x,c}^{\text{DF,nonlocal}}$, omitted α implies $\alpha = 1$
- X=exchange, C=correlation, DF=density functional
- SR/LR=short/long-range, ω is range separation parameter*

* In $E^{\text{SR,LR}}$ Coulomb potential is multiplied by $\text{erfc}(\omega r)$ and $\text{erf}(\omega r)$ respectively

* In Gaussian 09 different ω can be used for SR/LR and HF/X-DF/C-DF

BUT the ugly part: DFT heads the wrong way

Science 2017, DOI: [10.1126/science.aah5975](https://doi.org/10.1126/science.aah5975)



Do not make these mistakes! (following Kieron Burke)

The Good: choose one functional of each kind and stick with it (e.g., LDA or PBE or B3LYP).

The Bad: Run several functionals, and pick 'best' answer.

The Ugly: Design your own functional with 2300 parameters.

Typical errors (the road to 'chemical' accuracy 1kcal/mol)

Table 8.1 Mean absolute errors and maximum errors, where available, in atomization energies for different methods over several different test sets (kcal mol⁻¹)

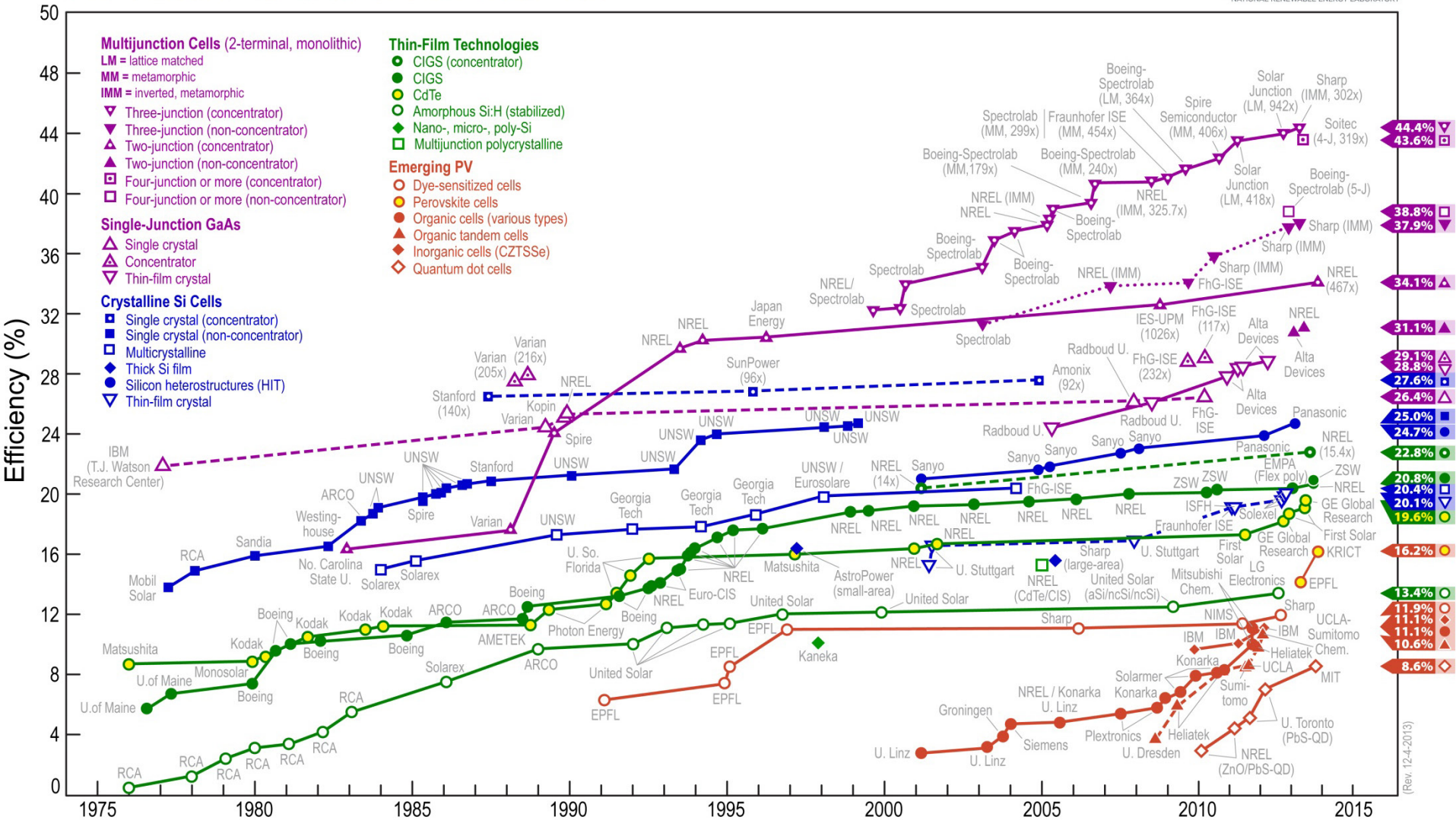
Level of theory	Test sets ^a				
	A	B	C	D	E
MO theoretical methods					
MNDO				9.3 (116.7)	
AM1				7.8 (58.2)	
PM3				7.0 (32.2)	
HF/6-31G(d,p)			119.2		
HF/6-311G(2df,p)	82.0		146.2 ^b		
HF/6-311+G(3df,2p)		74.5 (170.0)	144.4 ^b	148.3 ^c (344.1)	211.5 ^c (582.2)
MP2/6-31G(d)	22.4	16.0 (40.3)	38.1 ^b		
MP2/6-31G(d,p)	23.7		22.0		
MP2/6-311+G(3df,2p)		7.3 (25.4)	9.7 ^b		
MP4/6-31G(2df,p)			13.5 ^b		
QCISD/6-31G(d)	28.8		51.7 ^b		
MC-QCISD			1.7 ^b		
CCSD(T)/6-311G(2df,p)	11.5				

Typical errors (the road to 'chemical' accuracy 1kcal/mol)

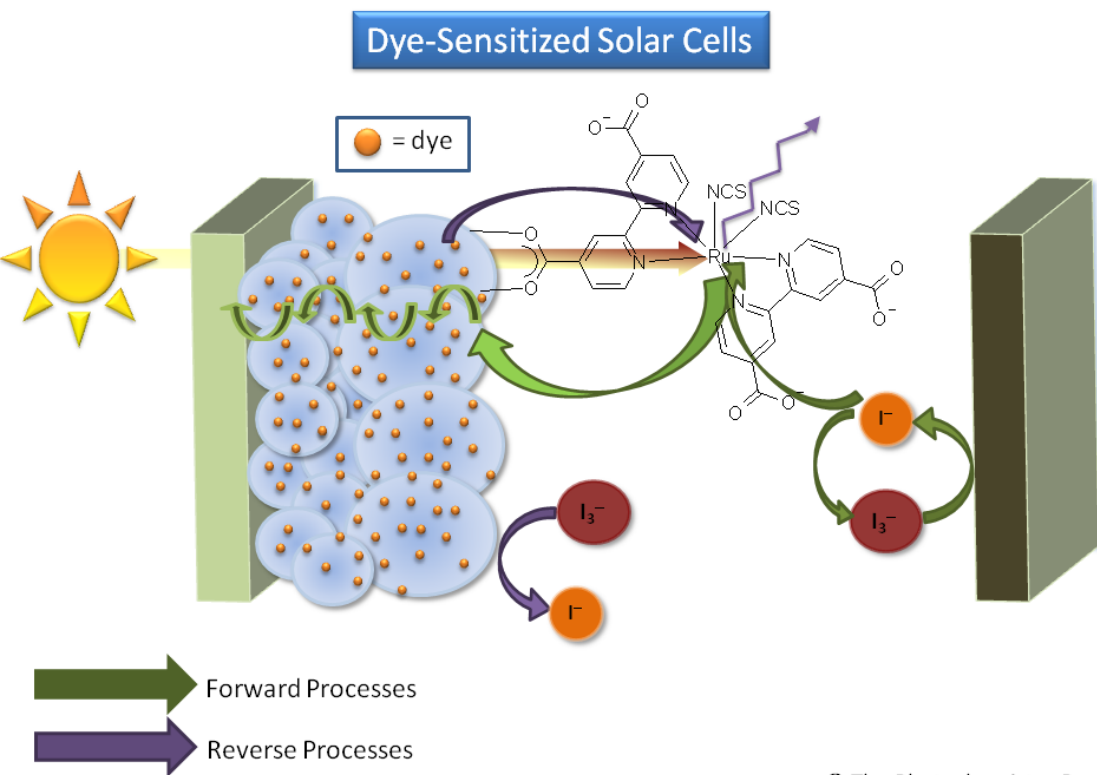
Level of theory	Test sets ^a				
	A	B	C	D	E
LSDA functionals					
SVWN/6-31G(d)	35.7	36.4 (84.0)		83.8	
GGA and MGGA functionals					
BLYP/6-31G(d)	5.6	5.3 (18.8)			
BLYP/6-31G(d,p)			7.0		
BLYP/6-31+G(d)		4.4			
PBE/6-311+G(3df,2p)		8.2 (29.1)		16.9 ^c (50.5)	22.2 ^c (79.7)
Hybrid functionals					
B3P86/6-311+G(3df,2p)		7.8 (22.7)		18.2 ^c (48.1)	26.1 ^c (79.2)
PBE1PBE/6-311+G(3df,2p)		3.1 (10.7)	4.4 ^b	4.9 ^c (21.3)	6.7 ^c (35.6)
TPSSh/6-311++G(3df,3pd)				4.2 ^c (22.0)	3.9 ^c (16.2)
B3LYP/6-311+G(3df,2p)		2.4 (9.9)		3.1 (20.2)	4.8 (21.6)

Case study 3: Binding energies

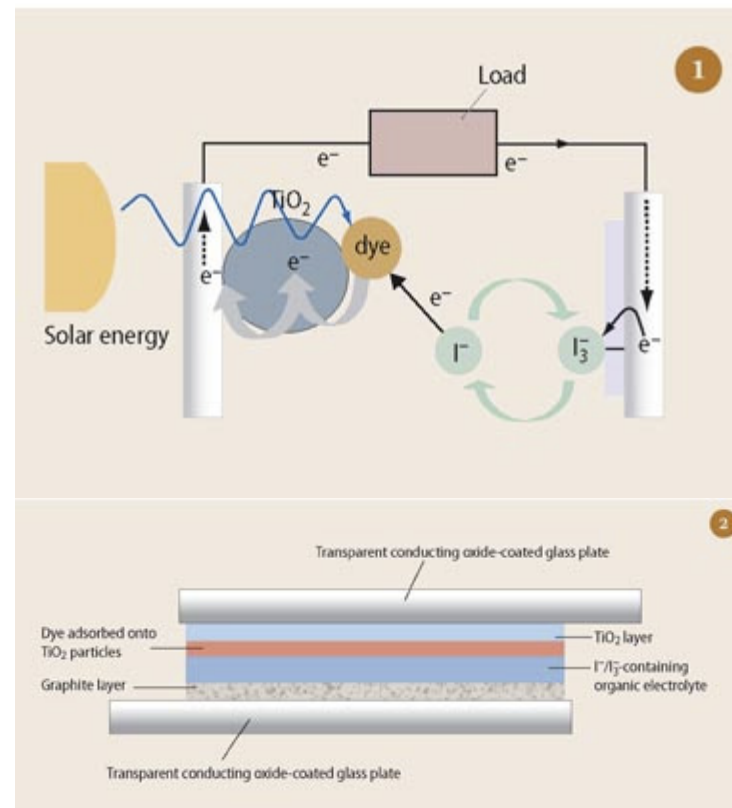
Best Research-Cell Efficiencies



Case study 3: Binding energies



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Forward and reverse electronic pathways in a dye-sensitized (Gratzel) solar cells

Can we replace Pt with something else?

Disadvantages:

- Use of liquid electrolyte;
- Ru is expensive;
- Pt is expensive.

Case study 3: Binding energies

Received 15 May 2012 | Accepted 25 Jan 2013 | Published 12 Mar 2013

DOI: 10.1038/ncomms2547

Rational screening low-cost counter electrodes for dye-sensitized solar cells

Yu Hou^{1,*}, Dong Wang^{2,*}, Xiao Hua Yang¹, Wen Qi Fang¹, Bo Zhang^{1,3}, Hai Feng Wang², Guan Zhong Lu², P. Hu^{2,4}, Hui Jun Zhao⁵ & Hua Gui Yang^{1,5}

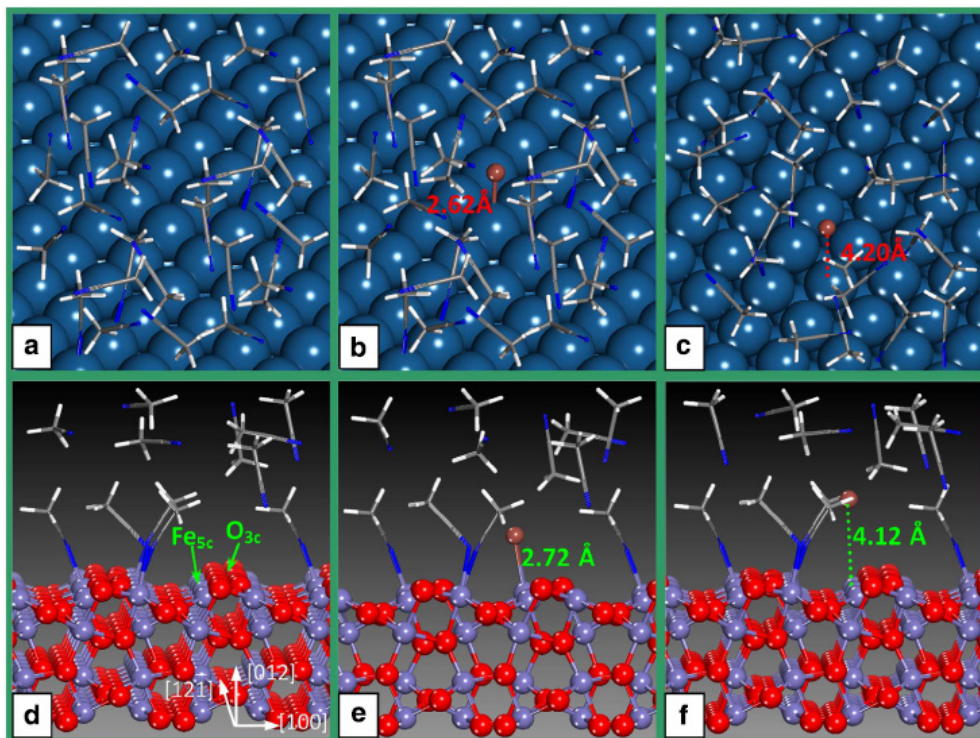


Figure 2 The related structures involved in IRR and energy profiles. (a–c) Pt(111) surface structure in the presence of CH₃CN solvent, I adsorption structure and the transition-state structure. (d–f) For the α-Fe₂O₃(012) surface.

Methods used: Density Functional Theory (DFT) & VASP

November–December, 2020

Computational Chemistry and Materials Modeling

Catalytic reaction on Pt surface:



Binding (adsorption) energy of I to Pt surface is critical for catalysis

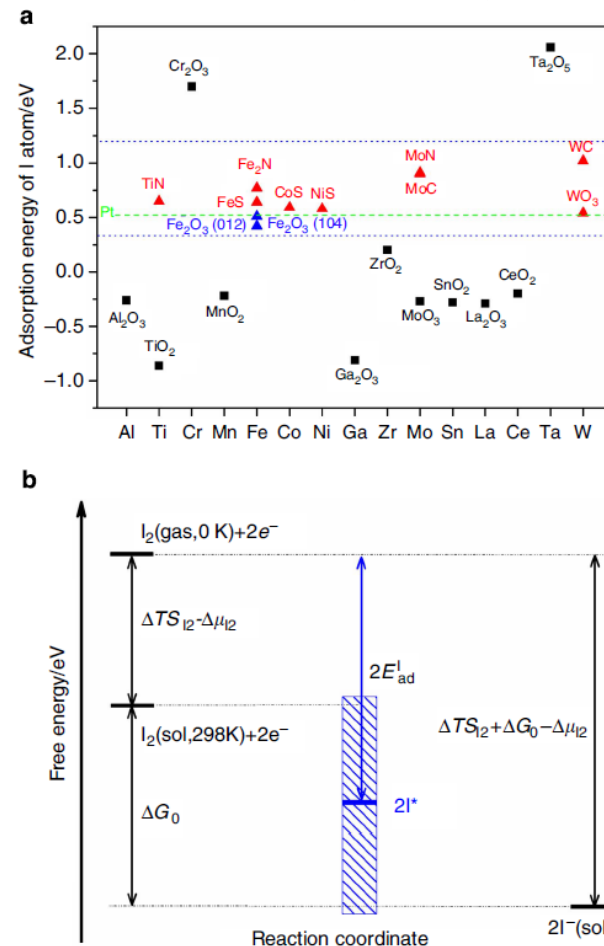


Figure 1 | Calculated adsorption energy of I atom on various compounds

Case study 3: Binding energies

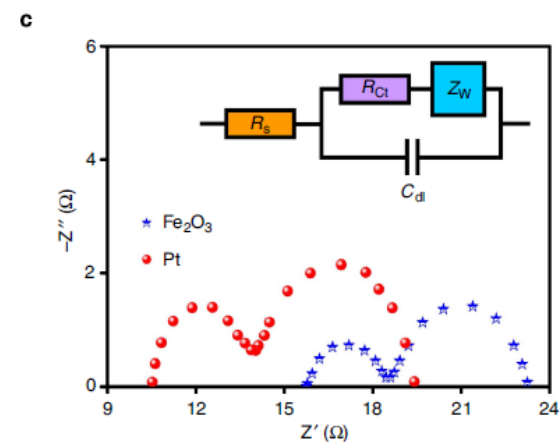
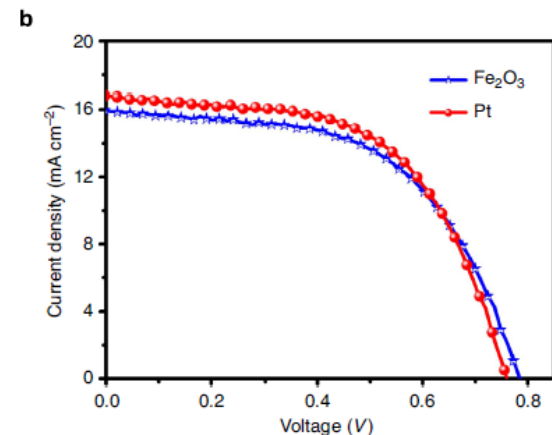
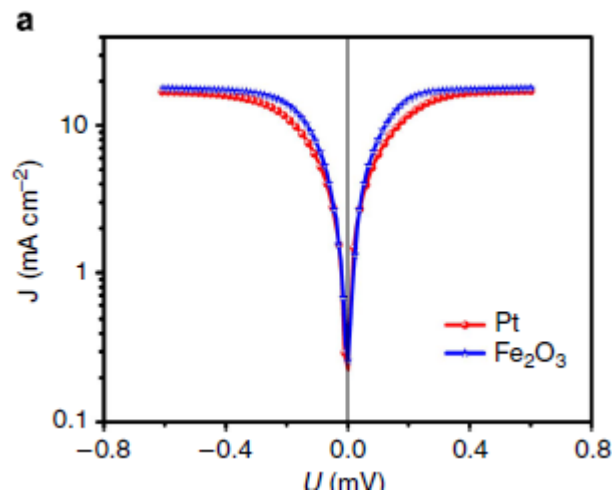
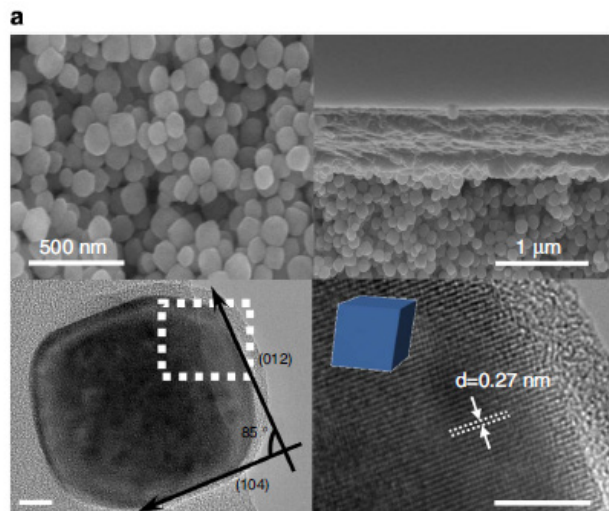
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Rational screening low-cost counter electrodes for dye-sensitized solar cells

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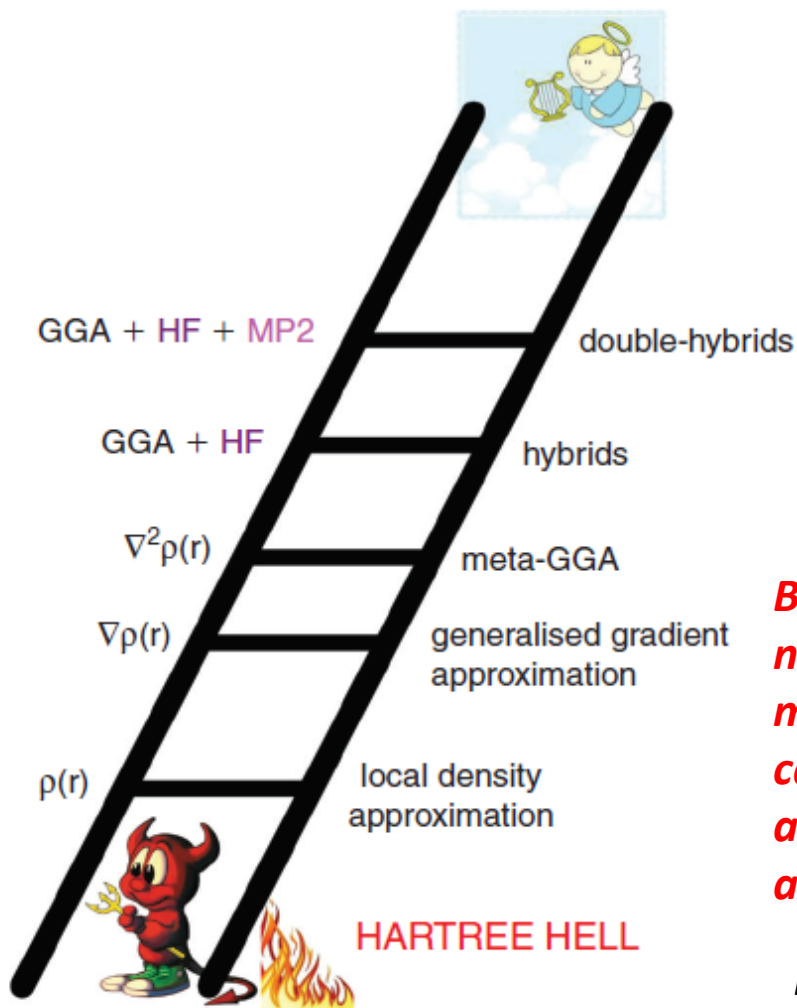
Experimental results for Fe_2O_3



- $\alpha-Fe_2O_3$ can be expected to replace the expensive Pt in DSCs as a promising CE catalyst
- Combination of first-principle calculations and experimental techniques to achieve the rational design of low-cost and high-efficiency CE materials for DSCs

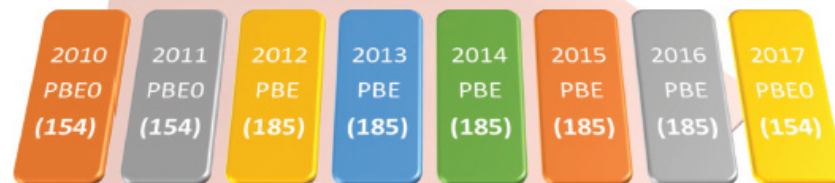
DFT conclusion

HEAVEN OF CHEMICAL ACCURACY



The (modified) Jacob's Ladder

DFT Poll Champion of the Year



Bottom line: Density Functional Theory is a great but necessarily approximate method. It is must to master as computational materials scientist. DFT can accomplish a lot and can fail badly. Use this approach with care: this is not “ab ignition” but “an approximate method derived from first principles”

L. Goerigk and N. Mehta, “A Trip to the Density Functional Theory Zoo: Warnings and Recommendations for the User” *Aust. J. Chem.* 2019, 72, 563–573

Discussion

1. Can you apply LDA or GGA functionals to describe insulators? Why? Is there better alternatives?
2. Can you apply Hartree-Fock to describe metals? Why? Is there a better alternatives?
3. Why hybrid DFT is so popular?
4. Explain GGA joke "...the gradient of the density differentiates between bond types..."
Brett: *snickers* "The gradient differentiates..."

Individual studies:

- **Reading.**

Required: Cramer (8.1-8.6)

Additional: Jensen (Ch.6).

Kieron Burke webpage – fantastic resource about DFT,

<http://dft.uci.edu/research.php#theabcofdft>

Slides DFT intro by Burke <http://dft.uci.edu/doc/tutorialKB.pdf>

Perspective on density functional theory

Kieron Burke

THE JOURNAL OF CHEMICAL PHYSICS **136**, 150901 (2012)

For your educational development (strongly recommended!)

<http://dft.uci.edu/research.php#theabcofdft>

<https://dft.uci.edu/pubs/PGB15b.pdf> DFT: A Theory Full of Holes?

ALSO review <https://link.aps.org/doi/10.1103/RevModPhys.87.897>

The ugly: DFT heads the wrong way:

Science 2017, DOI: [10.1126/science.aah5975](https://doi.org/10.1126/science.aah5975)

DFT: The most popular electronic structure method

(No. of ISI citations per year that contain the keywords 'density functional or DFT' resp. 'Hartree and Fock' or 'coupled cluster')

