

Chemically Biased Intro to The Density Functional Theory

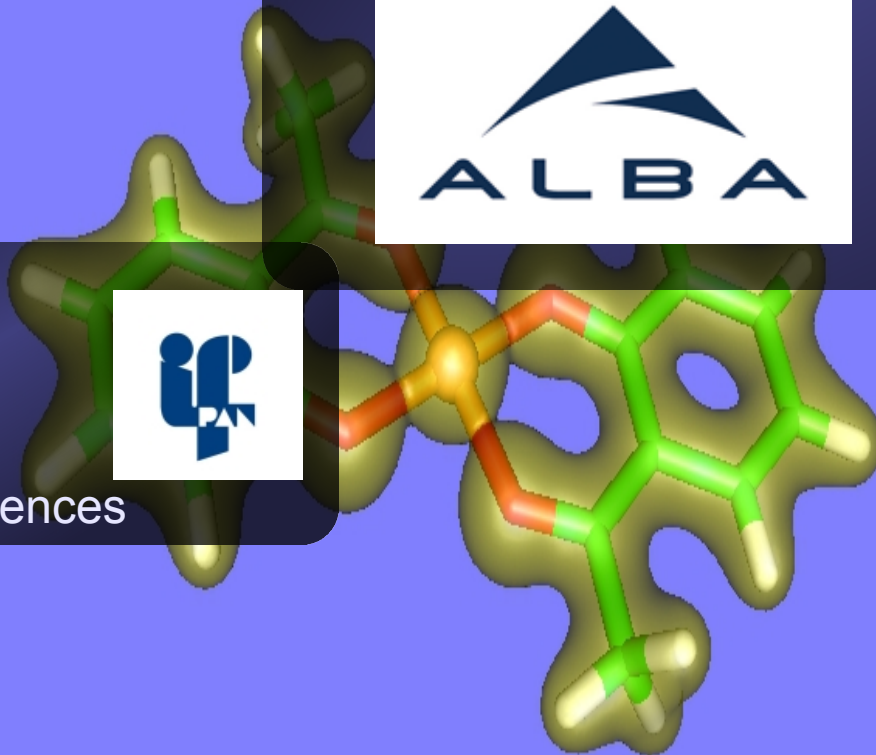
Introduction to Molecular Modeling



Paweł Rejmak

Institute of Physics

Polish Academy of Sciences



The Previous Talk in 3 Slides (1)

- ❏ **Hartree-Fock method** is variational search for the best approximation to the unknown, N-electron wavefunction in a form of **Slater determinant** made of N 1-electron wavefunction called **spinorbitals**.

$$E_{HF} = \min \langle \Psi_{SD} | \hat{H}_e | \Psi_{SD} \rangle$$

$$\Psi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{q}_1) & \varphi_1(\mathbf{q}_2) & \cdots & \varphi_1(\mathbf{q}_N) \\ \varphi_2(\mathbf{q}_1) & \varphi_2(\mathbf{q}_2) & \cdots & \varphi_2(\mathbf{q}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(\mathbf{q}_1) & \varphi_N(\mathbf{q}_2) & \cdots & \varphi_N(\mathbf{q}_N) \end{vmatrix}$$

$$\varphi_i(\mathbf{q}_p) = \varphi(\mathbf{r}_p, \sigma_p), \quad \langle \varphi_i(\mathbf{q}_p) | \varphi_j(\mathbf{q}_p) \rangle = \delta_{ij}, \quad \langle \Psi_{SD} | \Psi_{SD} \rangle = 1$$

$$\hat{H}_e = \sum_i \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I,i} -\frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} \left(+ \sum_{I>J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} = \text{const.} \right)$$

The Previous Talk in 3 Slides (2)

- ❑ Minimization of $\langle \Psi_{SD} | \hat{H}_e | \Psi_{SD} \rangle$ leads to set of N 1-el. (pseudoeigenvalue) **Fock equations**, which must be solved iteratively → **Self Consistent Field (SCF)** procedure.
- ❑ To make Fock equations solvable in practice, one has to expand SO in certain known, finite, thus incomplete **basis set**. The quality of HF & post-HF results depends on the type & size of the basis functions.
- ❑ Byproduct of HF is set of 1-el. spinorbitals (SO), they & their eigenvalues should be interpreted with caution.
- ❑ HF predicts pretty good geometries & IR freqs. at least for closed shell molecules. Energetics (ΔE of chemical reaction, electronic excitations) are not so good, often very bad.
- ❑ Why? HF method is **mean field approximation**, namely each electron interacts with the average electric field created by (N-1) remaining electrons. But electrons should interact one with another, not by mean field.

The Previous Talk in 3 Slides (3)

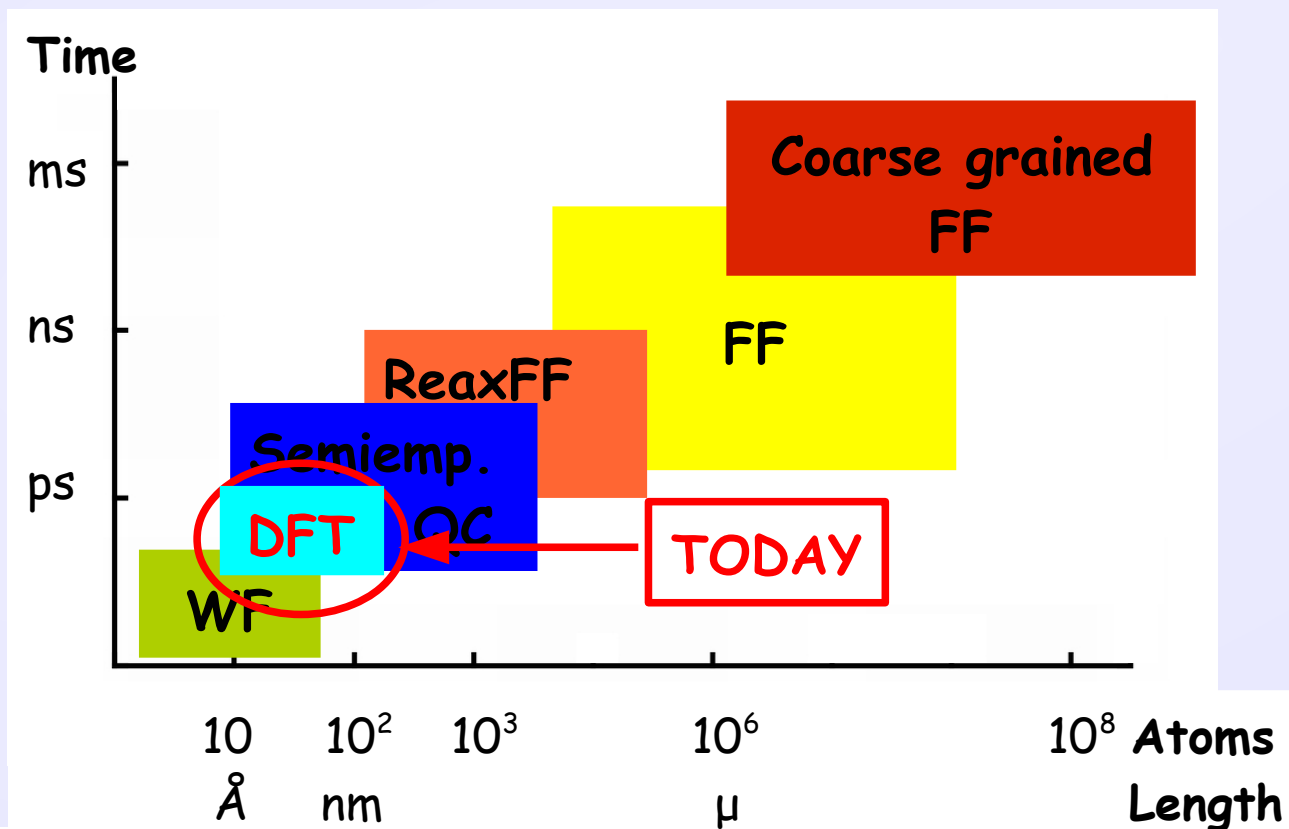
- HF method correctly describes, due to the antisymmetric form of SD, **exchange correlation**, i. e. between el. of the same spin.
- Coulomb correlation** is missing, due to the mean field treatment of e-e interactions.
- Correlation Energy** $E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} < 0$, large fraction of measurable ΔE .
- Coulomb correlation** can be roughly divided into (i) **dynamical** - el. move in a way to avoid each other, (ii) **static** - when N-el. WF can't be approx. by one SD.



- Configuration Interaction** method: the exact N-el. WF is represented as a linear combination of many SD.
- In practice **full CI** can be done for very small molecules (~ 10 electrons) & many approx. to it were developed. They are still computationally expensive and/or suffer from certain limitations. E. g. **MP2** method can be applied to moderate systems of ~ 100 electrons, but it describes dynamical correlation only.

Approches to Electron Energy

- Wavefunction (WF) based methods
- Density Functional Theory up to $\sim 10^2 - 10^3$ atoms
- Semiempirical/Tight Binding methods
- Molecular Mechanics



Functionals for Appetizer

- Functional is a $F[f]$ function, which arguments are functions & the values are numbers, e. g. arc length connecting (x_1, y_1) & (x_2, y_2)

$$L[f] = \int_{x_1}^{x_2} \sqrt{1 + f'(x)^2} dx$$

with domain $\{f\}$: $f(x_1)=y_1$ & $f(x_2)=y_2$, has minimum $f(x) = \left(\frac{y_2 - y_1}{x_2 - x_1} \right) (x - x_1)$

- Functional is **local**, if $f(x)$ for each x contributes independently to F , e. g.

$$F[f] = \int_{x_1}^{x_2} f(x)^m dx$$

otherwise is **nonlocal**, e. g.

$$G[f] = \int_{x_1}^{x_2} \int_{y_1}^{y_2} f(x) K(x, y) f(y) dx dy, \quad H[f] = \frac{\int_{x_1}^{x_2} f(x)^m dx}{\int_{x_1}^{x_2} f(x)^n dx},$$

- In QM mean E is functional of Ψ

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle \equiv \int_X \Psi^*(x) \hat{H} \Psi(x) dx$$

Electron (Probability) Density

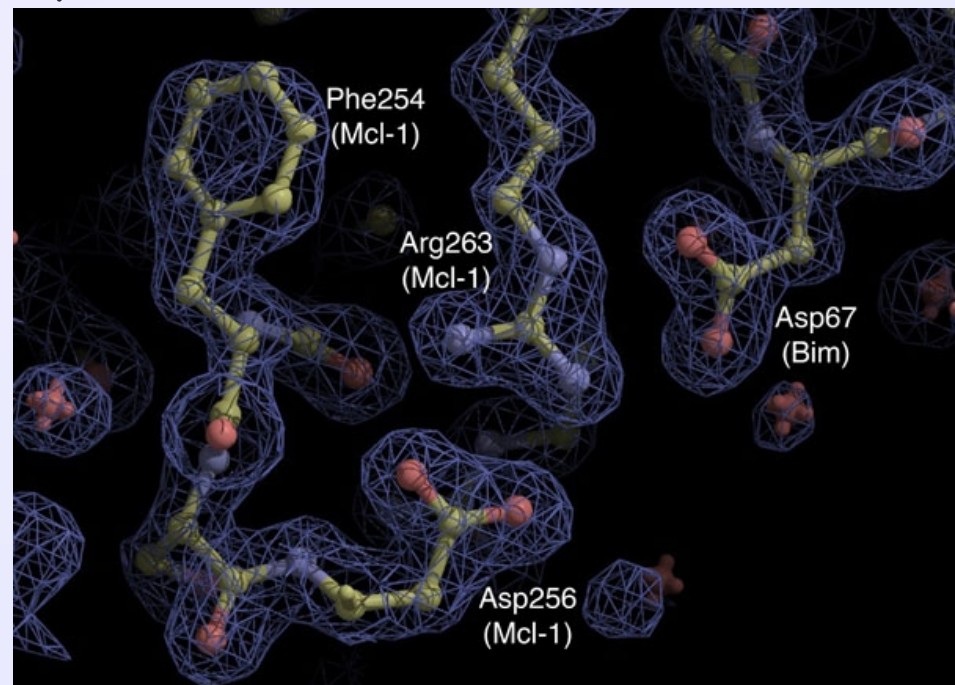
$$\rho(\mathbf{r}) = N \sum_{\sigma_i} \int |\Psi(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3 \dots \mathbf{q}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N, \quad \mathbf{x} = (\mathbf{r}, \sigma)$$

$$\left(\equiv \langle \Psi | \hat{\rho} | \Psi \rangle, \quad \hat{\rho} = \sum_{i=1}^N \sum_{\sigma_i} \delta(\mathbf{r} - \mathbf{r}_i) \right)$$

▣ $\rho(\mathbf{r}) \geq 0 \quad \wedge \quad \text{for finite systems:} \quad \rho(\mathbf{r} \rightarrow \infty) = 0 \quad \wedge \quad \int_{\text{all space}} \rho(\mathbf{r}) d\mathbf{r} = N$

▣ $\rho(\mathbf{r})$ is much nicer creature than Ψ - it lives in our 3D physical space, instead of $4N$ spin-position space & is observable, can be "seen" in diffraction experiments.

Fig. from Czabotar & co. *PNAS*, 2007, 104, 6217.



In The Beginning...

- Idea to represent E (or its part) as a functional of electron density $\rho(\mathbf{r})$ is almost as old as Schrödinger equation (1926).

- Thomas-Fermi model for homogeneous electron gas (1927)

$$E_{TF} = \underbrace{C_{TF} \int \rho(\mathbf{r})^{5/3} d\mathbf{r}}_{T_{TF}} + \underbrace{\int v_{ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}}_{\text{interaction with external potential}} + \underbrace{\int \int \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2}_{\text{classical Coulomb energy}}$$

- + Dirac term for exchange energy (lowering of effective repulsion between el. of the same spin due to Pauli exclusion) $K_D \propto \int \rho(\mathbf{r})^{4/3} d\mathbf{r}$

- TF model has some success in (qualitative) atomic & solid state physics, but it fails to describe chemical bonding.

- von Weizsäcker correction to T_{TF} $T_W \propto \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r}$

gives qualitative description of chemical bonds, but results still not impressive.

- Generally, it's hard to find a robust expression for $T[\rho]$.

Make Hartree-Fock Easier

❏ Xa method (Slater 1951):

$$\hat{f}(1)\chi_a(1) = \left\{ \hat{h}(1) + \sum_{b \neq a}^N (\hat{J}_b(1) - \hat{K}_b(1)) \right\} \chi_a(1)$$

$$\hat{h}(1) = -\frac{1}{2} \nabla^2(1) + \sum_I \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_1|}, \quad \hat{J}_b(1) = \left\langle \chi_b(2) \left| \frac{1}{r_{12}} \right| \chi_b(2) \right\rangle = \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2$$

$$\hat{K}_b(1)\chi_a(1) = \left\langle \chi_b(2) \left| \frac{1}{r_{12}} \right| \chi_a(2) \right\rangle \chi_b(1) \rightarrow \hat{K}_{Slater} = const \cdot \alpha \int \rho(\mathbf{r}_1)^{\frac{1}{3}} d\mathbf{r}_1$$

$$\alpha \in \langle 2/3, 1 \rangle$$

❏ Xa method gives HF quality results (or worse), but is much faster computationally ($\sim K^4$ exchange integrals avoided). It was quite popular in computational physics & chemistry in 60's-80's, including modeling of solids or medium size molecules.

Hohenberg-Kohn Theorems

- ❑ But it was until 1964, when the use of density functionals was legalized:
- **HK1** External* potential is uniquely determined (up to additive constant) by the ground state density of particles.

$$\rho_1(\mathbf{r}) \neq \rho_2(\mathbf{r}) \Rightarrow v_1(\mathbf{r}) \neq v_2(\mathbf{r})(+const.)$$

Consequently $\rho(\mathbf{r})$ determines Ψ_{GS} , thus E & any observables.

$$\rho(\mathbf{r}) \Rightarrow v_{ext}(\mathbf{r}) \Rightarrow \Psi(\mathbf{r}, \sigma)$$

*External means not coming from considered particles, like nuclear potential for electrons in molecules & solids.

- **HK2** If $E_v[\rho]$ is functional dependence of E on ρ for a given external potential v , then for any N -particle trial density:

$$E_v[\rho_{trial}] \geq E_v[\rho_{exact}] = E_{GS}$$

(due to Ritz-Rayleigh variational principle for Ψ & because $\Psi = \Psi[\rho]$).

- ❑ Initial HK proof was only for special class of ρ , but it was extended to more general cases soon.

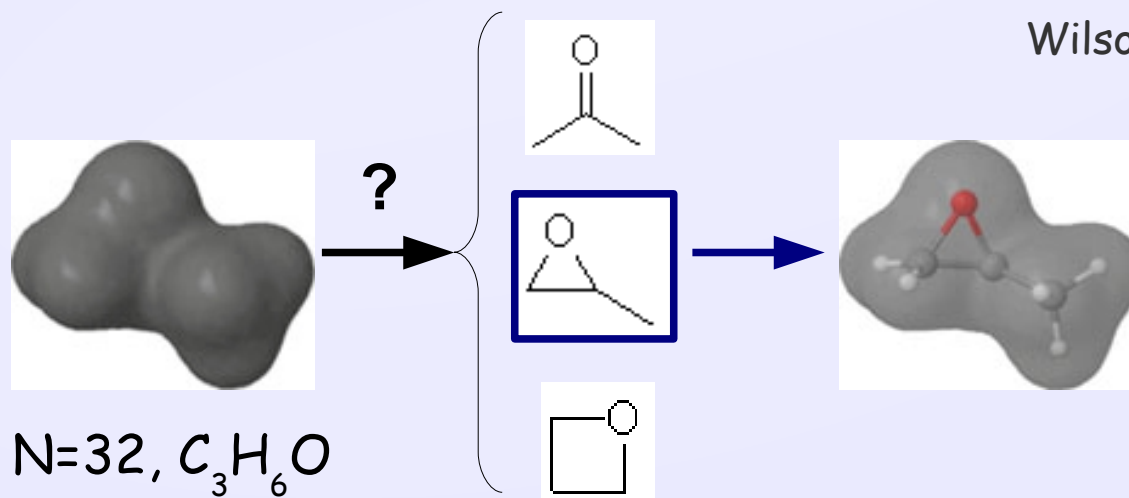
Hohenberg & Kohn *Phys. Rev.* **1964**, 136, B864; Lieb & Levy *PNAS* **1979**, 76, 6062.

More on Hohenberg-Kohn Theorems

- ❑ The consequence singularity of Coulomb potential in the position of point charge, el. density obeys Kato's cusp condition

$$\lim_{r \rightarrow R_I} \frac{1}{\rho(\mathbf{r})} \frac{\partial \rho(\mathbf{r})}{\partial r} = -Z_I$$

- ❑ Furthermore $\int \rho(\mathbf{r}) d\mathbf{r} = N$
- ❑ Knowing $\rho(\mathbf{r})$ we know no. of electrons, positions & charges of nuclei, thus we know full (nonrelativistic, Born-Oppenheimer approx.) \hat{H} .



Wilson JCP 1962, 36, 2232.

Fig. after Jacobsen & Cavallo "Directions For Use DFT..." in "Handbook of Computational Chemistry Vol. 1" Springer, 2012.

Kohn-Sham Method

- HK proofs are existence theorems, they say nothing about finding $E[\rho]$.
- Kohn-Sham idea: consider fictional system of N noninteracting fermions (kohnshamions?) in certain external $v_s(\mathbf{r})$ & having the same $\rho(\mathbf{r})$ as the real system of N interacting electrons. Kohn & Sham *Phys. Rev.* **1965**, 140, A1133.

$$\hat{H}_s = \sum_i \hat{h}_s(\mathbf{r}_i) = \sum_i \left(-\frac{1}{2} \nabla_i^2 \right) + v_s(\mathbf{r}_i)$$

$$\hat{h}_s(\mathbf{r}_i) \varphi^{KS}(\mathbf{q}_i) = \varepsilon_i \varphi^{KS}(\mathbf{q}_i), \quad (\mathbf{q}_i = (\mathbf{r}_i, \sigma_i))$$

$$\rho_s(\mathbf{r}) = \sum_i \left| \varphi^{KS}(\mathbf{q}_i) \right|^2 = \rho_{real}(\mathbf{r}), \quad \Psi_s = \det[\varphi_1(\mathbf{q}_1), \varphi_2(\mathbf{q}_2), \dots, \varphi_N(\mathbf{q}_N)]$$

$$E_s = \sum_i \varepsilon_i^{KS} = \langle \Psi_s | \hat{H}_s | \Psi_s \rangle = T_s[\rho] + V_s[\rho]$$

- T of noint. particles is exactly $T_s[\rho] = \sum_i \left\langle \varphi_i(\mathbf{1}) \left| -\frac{1}{2} \nabla_1^2 \right| \varphi_i(\mathbf{1}) \right\rangle$
- The existence of $v_s(\mathbf{r})$ producing $\rho_s = \rho_0$ has not been proved in general, but it was for many specific cases & no counterexample was found. Due to HK1 if $v_s(\mathbf{r})$ exists for given ρ , it is unique.

Exchange-Correlation Energy (& Potential)

$$\begin{aligned}
 E_{real}[\rho] &= T[\rho] + V_{ee}[\rho] + V_{ext}[\rho] = \quad (\mathbf{r}_i = \mathbf{i}) \\
 &\quad \quad \quad T_s[\rho] \quad \quad \quad J[\rho] \quad \quad \quad V_{ext}[\rho] \\
 &= \sum_i \left\langle \varphi_i(\mathbf{1}) \left| -\frac{1}{2} \nabla_1^2 \right| \varphi_i(\mathbf{1}) \right\rangle + \int \int \frac{\rho(\mathbf{1})\rho(\mathbf{2})}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + \int v_{ext}(\mathbf{1})\rho(\mathbf{1}) d\mathbf{r}_1 + \\
 &\quad \quad \quad + E_{xc}[\rho(\mathbf{1})]
 \end{aligned}$$

- ▣ $E_{xc}[\rho]$ covers all parts of T & V_{ee} which are not (1) kinetic energy of nonint. fermions $T_s[\rho]$ & (2) classical Coulomb energy $J[\rho]$.
- ▣ $T_s[\rho]$, being the largest part of $T[\rho]$, can be calc. exactly as $T_s[\varphi]$.
- ▣ It can be shown that our wanted $v_s(\mathbf{r})$ is:

$$v_s(\mathbf{1}) = \int \frac{\rho(\mathbf{2})}{r_{12}} d\mathbf{r}_2 + v_{ext}(\mathbf{1}) + v_{xc}(\mathbf{1}), \quad v_{xc}(\mathbf{1}) = \frac{\delta E_{xc}[\rho(\mathbf{1})]}{\delta \rho(\mathbf{1})}$$
- ▣ Search for total $E[\rho]$ is shifted to search for $E_{xc}[\rho]$ & (too) many approx. for the latter were proposed.

Kohn-Sham Method @ Work

- Minimizing $E[\rho]$ with respect to ρ/φ^{KS} leads to N 1-particle equations:

$$\hat{h}_s(\mathbf{1})\varphi_i(\mathbf{1}) = \left(-\frac{1}{2}\nabla_1^2 + v_s(\mathbf{1})\right)\varphi_i(\mathbf{1}) = \varepsilon_i\varphi_i(\mathbf{1}), \quad i=1, \dots, N$$

- $v_s(\mathbf{r})$ depends on $\rho(\mathbf{r})/\varphi^{\text{KS}}(\mathbf{r})$ itself, thus we have pseudoigenvalue problem, which must be solved iteratively, in similar way to HF.

- The rest is almost like Hartree-Fock-Roothan method:

- Specify molecule ($N, Z_{\text{I}}, R_{\text{I}}$) & basis set (& spin - see further)
- Guess ρ^0 (& calc. $E[\rho^0]$)
- Calculate $v_s[\rho^0(\mathbf{r})]$ & solve 1-particle eqs. for ε & φ^{KS}
- Calculate ρ^1 (or $E[\rho^1]$) from φ^{KS} & compare with initial one - if the same stop, if not calc. $v_s[\rho^1(\mathbf{r})]$ & ... etc

- In practice - φ^{KS} are expanded in known, finite basis set & the problem of finding φ/ρ is reduced to

finding expansion coefficients.

$$\varphi_i^{\text{KS}}(\mathbf{r}) = \sum_{\mu}^K C_{\mu i} \phi_{\mu}, \quad K \geq N$$

Kohn-Sham vs. Hartree-Fock

- ▣ **KS method is exact one!** If $E_{xc}[\rho]/v_{xc}[\rho]$ were known, one would know exact ρ & by putting it into $E_v[\rho]$, exact electron E !
 - ▣ HF method is approximated one from the very beginning - one looks for the best single determinant approx. to true N-electron WF.
 - ▣ KS method is genuine DFT approach, KS orbitals & determinant WF are kind of byproduct to get true ρ & E .
 - ▣ In both HF & KS we have set of pseudoeigenvalue 1-particle equations:

$$\left(-\frac{1}{2} \nabla_1^2 + v^A[\{\varphi_j^A\}] \right) \varphi_i^A(\mathbf{1}) = \varepsilon_i^A \varphi_i^A(\mathbf{1}), \quad A=HF, KS$$
 but in HF effective potential is nonlocal due to the presence of exchange term:

$$\hat{K}_b(2) \chi_a(1) = \left\langle \chi_b(2) \left| \frac{1}{r_{12}} \right| \chi_a(2) \right\rangle \chi_b(1)$$
- In KS $v_s(\mathbf{r})$ is (can be) local function of \mathbf{r} (although nonlocal functional of $\rho(\mathbf{r})$!), which makes life much easier.

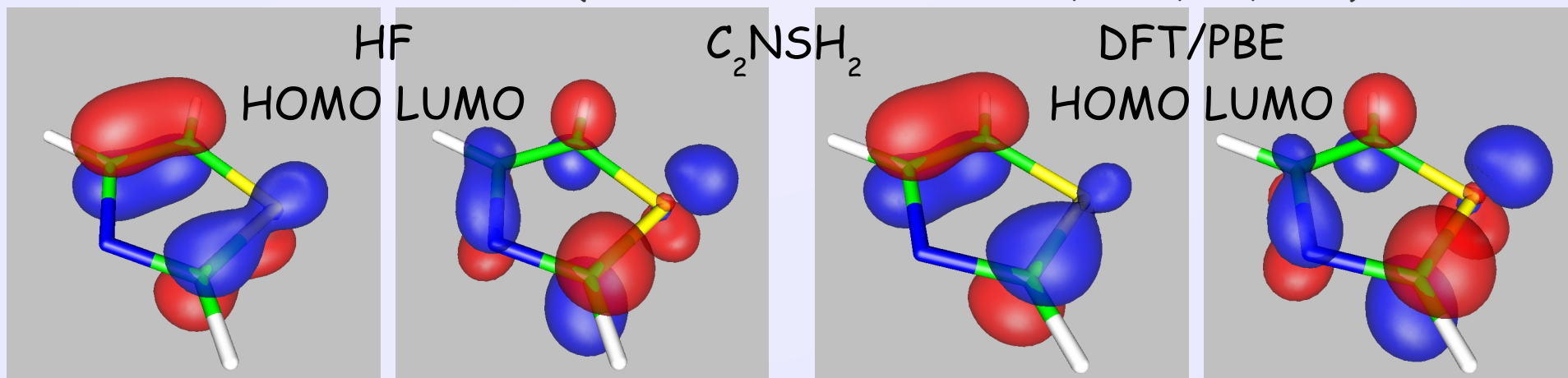
KS Orbitals & Orbital Energies

- Physical meaning of KS spinorbitals? - **none**, strictly speaking (like in HF).
- The exception is KS HOMO Janak's theorem: $\epsilon_{\text{HOMO}} = -\text{IP}$, but it's true for exact E_{xc} , approx. ones usually violates this theorem.

- Total E is not a sum of orbital energies! (it would 2x count interactions)

$$E_{\text{KS}} = \sum_i^{\text{occ.}} \epsilon_i - \frac{1}{2} J[\rho] + E_{\text{xc}}[\rho] - \int v_{\text{xc}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

- However, KS orbitals were shown to be useful for interpretation, often better than HF orbitals. (Stowasser & Hoffmann *JACS*, 1999, 121, 3414)



- Unlike in HF, in KS both occupied & virtual orbitals experience correct (N-1) el. potential, resulting in better description of excited states.

What is E_{xc} Made From?

$$E_{xc}[\rho] = (V_{ee} - J) + (T - T_s) < 0, \quad J[\rho] = \int \int \rho(\mathbf{1}) \rho(\mathbf{2}) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2$$

$$T_s[\rho] = \sum_i \left\langle \varphi_i^{KS}(\mathbf{1}) \left| -\left(\frac{1}{2}\right) \nabla^2 \right| \varphi_i^{KS}(\mathbf{1}) \right\rangle$$

➤ E_{xc} is made from:

- 1 (Coulomb) correlation contribution to $V_{ee}[\rho]$ (<0).
- 2 Exchange (correlation) contribution to $V_{ee}[\rho]$ (<0).
- 3 (Coulomb) correlation contribution to $T[\rho]$ (>0).

➤ E_{xc} is for:

- A** accounting for (Coulomb) correlation between el.
- B** accounting for exchange (correlation) between el. of the same spin
- C** removal of artificial el. self-interaction from $J[\rho]$ term.

HF has exact B & C (K integrals), but no A. Available DFT variants have A-C approx.

Jacobb's Ladder

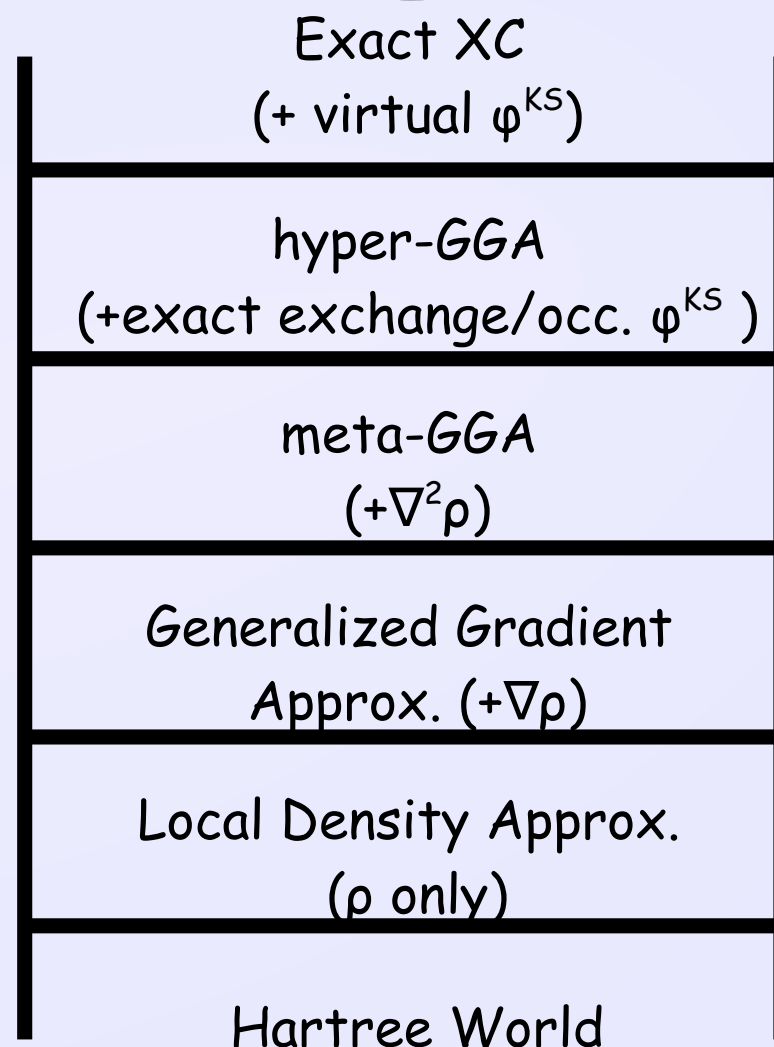
Genesis 28, 10-19 & John Perdew



Michael Willmann 'Landscape with Jacobb's Dream', ~1691, Gemäldgalerie, Berlin

Chemical accuracy $\Delta E \sim 0.01$ eV

Heaven of Chemical Accuracy



1st Rung: Local Density Approximation (LDA)

- ❑ $E_{XC}^{LDA}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{XC}[\rho(\mathbf{r})] d\mathbf{r} = \int \rho(\mathbf{r}) \{ \varepsilon_X[\rho(\mathbf{r})] + \varepsilon_C[\rho(\mathbf{r})] \} d\mathbf{r}$
where ε_{XC} is E_{XC} density (per particle).
- ❑ ε_X is $\rho^{1/3}$, thus we got Slater-Dirac functional.
- ❑ ε_C bit more lengthy, analytical expressions known only for high & low density limits. Very accurate interpolation is known from fitting to Monte-Carlo simulations of homogenous gas for different ρ .
- ❑ LDA is exact approach for homogenous gas, thus it works best for simple metals. Nevertheless, it has (surprisingly) good performance for other solids & (even) molecules.
- ❑ LDA predicts pretty accurate geometries & IR freqs., slightly too short bonds. Energetics is worse, LDA overestimates bondings.
- ❑ Spectacular failures of LDA - wrong order of phase transition, incorrect magnetic phases, e. g. for Fe nonmagnetic fcc phase predicted more stable than magnetic bcc ferromagnetic.

2nd Rung: Generalized Gradient Approximation (GGA) & 3rd Rung: meta-GGA

$$E_{XC}^{GGA}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{XC}^{GGA}[\rho(\mathbf{r}), \nabla \rho(\mathbf{r})] d\mathbf{r} = \int \rho(\mathbf{r}) \left\{ \varepsilon_X^{GGA} + \varepsilon_C^{GGA} \right\} d\mathbf{r}$$

Simple gradient expansion was shown to spoil LDA results, additional constraints had to be imposed on gradient corrected ε_{XC} , this is **GGA**.

- ▶ GGA is generally much better than LDA, clearly better energetics. Currently GGA is a kind of 'standard DFT'.
- ▶ GGA overcorrelates electrons a bit, thus giving a bit too long bonds/too low bonding energies.
- ▶ GGA is formally still local functional! Contribution to E_{GGA} in point \mathbf{r} depends only on the values of ρ & $\nabla \rho$ at this point. It is referred to as **semilocal**, because $\nabla \rho$ depends on the ρ in $\mathbf{r}+d\mathbf{r}$.

$$E_{XC}^{meta-GGA}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{XC}^{GGA}[\rho(\mathbf{r}), \nabla \rho(\mathbf{r}), \nabla^2 \rho(\mathbf{r})] d\mathbf{r}$$

Simple gradient expansion was shown to spoil LDA results, additional constraints had to be imposed on gradient corrected ε_{XC} , this is **GGA**. The next step is to take $\nabla^2 \rho$, or (almost) equivalently density of kinetic energy. **Meta-GGA** offers moderate improvement to GGA results & is moderately popular (historically 4th step was developed before 3rd one).

What is Wrong with (Semi)Local E_{xc} ?

❏ Main issues are:

- ▶ Negative ions & highly excited electronic states are not bound.
- ▶ No van der Waals interactions, *i. e.* no interactions between non-overlapping ρ (hydrogen bonds are qualitatively OK in GGA).
- ▶ Too strong delocalization of d and f (particularly $3d$ & $4f$) electrons: too small or no gaps in Mott insulators, overstabilization of low spin states = (semi)local DFT overcorrelates strong correlation cases.

❏ This is generally due to the wrong asymptotic behavior of $v_{xc}(\mathbf{r})$. In finite systems, for $|\mathbf{r}| \rightarrow \infty$ v_{xc} should $\rightarrow (-1/|\mathbf{r}|)$, instead in (semi)local approx. it decays exponentially with r , just like $\rho(\mathbf{r})$.

❏ To overcome this problems one needs nonlocal $E_{xc}[\rho]$. This is typically achieved by making E_{xc} explicit functional of KS orbitals.

4th & 5th Rungs: Here Comes Orbitals Again

▣ 4th rung (hyper-GGA, XX) should include (partially) exact exchange.

► The (only) widely applied variant of XX are **hybrid functionals**

$$E_{XC}^{hybrid}[\rho] = E_C^{(meta)GGA}[\rho] + aE_X^{(meta)GGA}[\rho] + (1-a)E_X^{exact}[\varphi_{occ}^{KS}], \quad a \in (0,1)$$

where $E_X^{exact}[\varphi_{occ}^{KS}]$ is a sum of exchange integrals (like in HF).

► Why not full HF-like exchange? Because mixing full exact exc. with approx. corr. spoils overall E_{xc} performance. Typically a is 0.2-0.5.

► Hybrids often perform much better than LDA & GGA, e. g. for strongly correlated systems. But admixture of HF can spoils cases of strong static correlation!

► Hybrids are computationally heavier than LDA & GGA, just like HF.

▣ 5th rung should include (partially) exact correlation, namely E_{xc} should be explicit functional of unocc. KS orbitals (e. g. MP2-like expression for E_c). As yet such functionals are not 'standard method'; they are also more computationally expensive than 'standard' DFT.

To Fit Or Not To Fit

❏ How to design $E_{xc}[\rho]$? 2 schools:

- ▶ (1) rely only on known exact conditions, which should be fulfilled by the exact $E_{xc}[\rho]^*$.
- ▶ (2) rely on above & adjust certain parameters to exp. data/results of highly accurate WF calc. for model systems.

❏ At 80's & 90's approach (2) was quite common, currently there is shift to more elegant (1) 'constraint satisfaction' approach.

Partially because DFT expanded from physics to chemistry & in quantum chemistry community 'semiempirical' is a bad word, but also because of limited transferability of empirical fitting.

❏ Most of current 4th & 5th rung functionals employs fitted parameters.

* Note that good performance of LDA is due to the fact, that LDA fulfill several important constraints the exact XC-functional does.

Functional Zoo

- There are (too) many of approximated $E_{xc}[\rho]$, names are typically acronyms of the authors:



Fig. from Burke

J. Chem. Phys. **2012**, *136*, 150901.

- ❑ B3LYP hybrid gained huge popularity in (organic) chemistry (in 2007 80% of DFT citations) - but it is not flawless, even for main group elements.
- ❑ Hybrid-meta-GGA M06 is gaining popularity in recent years.
- ❑ Pretty good & empirical parameter free are gradient PBE & hybrid PBE0.

Making Shortcuts in DFT

➤ Many solutions to specific DFT problems proposed.

➤ **Van der Waals interactions:**

➤ The simplest approach to account for them is semiempirical **DFT-D**

$$E_{DFT-D} = E_{DFT} + \sum_{AB} f_{damp}(R_{AB}) \frac{C_{AB}}{R_{AB}^6}, \quad R_{AB} \rightarrow 0 \Rightarrow f_{damp}(R_{AB}) \rightarrow 0$$

C_{AB} fitted to exp. data (e. g. polarizabilities) or MP2 results, correction can be added to any 'normal' DFT.

➤ Adding nonlocal part to (semi)local EXC. This term is calc. in non-SCF manner, thus increase in computation time negligible.

$$E_{DFT+nonloc} = E_{DFT} + \int \int \rho(\mathbf{r}_1) \varphi(\mathbf{r}_1, \mathbf{r}_2) \rho(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

Grimme *WIREs Comp. Mol. Sci.* **2011**, 1, 211; Klimeš & Michaelides *JCP* **2012**, 137, 120901.

➤ **DFT+U for strongly correlated d & f electrons:** in solid state physics it is often expressed by explicitly orbital dependent term, which strength is controlled by empirical U parameter.

see for example Himmetoglu & co. *Int. J. Quantum Chem.* **2014**, 114, 14.

Density or Spin Density? (H_2 Strikes Back)

- ❑ In non-relativistic case \hat{H} is not spin dependent & HK guarantees, that E is the functional of ρ only, even for spin polarized case. Formally we do need functional of spin densities ρ^a, ρ^b only in relativistic case.
- ❑ In practice, approx. $E_{xc}[\rho^a, \rho^b]$ are shown to work better than approx. $E_{xc}[\rho]$. This leads to unrestricted & restricted KS methods (like in HF).

❑ H_2 dissociation:

singlet H_2 should break into

2 singlet H atoms (1/2 α & β spin at each),
but approx. RKS can't do it.

UKS gives correct dissociation curve,
but breaks spin symmetry ($H^a + H^b$).

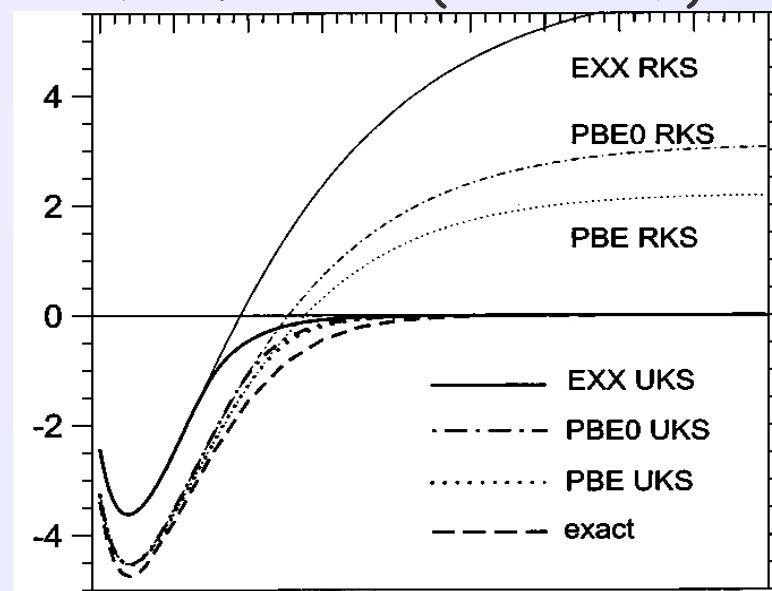


Fig from Fuchs et al. *JCP* **2005**, 122, 094116.

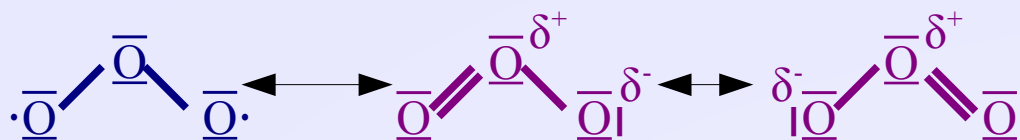
- ❑ Pragmatic approach: enjoy accurate E vs R curve & do not think too much about incorrect spin densities.

Why Do We Like DFT & KS?

- ☑ Simply, it is correlated method with computational cost of HF (or less).
- ☑ For strongly correlated systems, like transition metals, HF practically always fails, DFT often gives good results.
- ☑ DFT is the only correlated method applicable to wide class of solids, both metals & semiconductors.
- ☑ Scaling of (semi)local DFT with basis set size K ($\sim N_{el}$) can be done even more favorable than of HF. Orbital dependent exchange operator in HF leads to $\sim K^4$ 2-el. integrals $\langle \mu(1) \nu(2) | r_{12}^{-1} | \lambda(1) \sigma(2) \rangle$, KS potential is only ρ dependent, thus if one expands ρ in auxiliary basis set $\rho = \sum_{\alpha} C_{\alpha} \tilde{\phi}_{\alpha}$ one has only $\sim K^3 \langle \mu(1) | r_{12}^{-1} | \alpha(2) \lambda(1) \rangle$ integrals.
- ☑ DFT is also less demanding about the quality(size) of basis set than traditional quantum chemistry methods.
- ☑ That's why Walter Kohn got the Nobel Prize in chemistry in 1998.

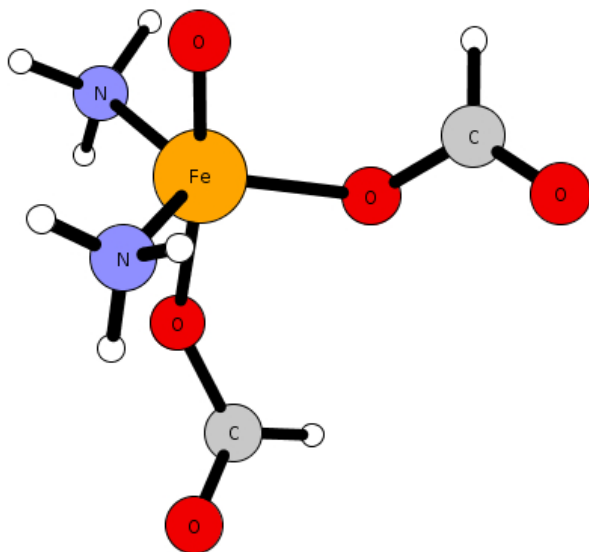
Just A Little DFT Show-Off

Harmonic O_3 frequencies (Jensen "Introduction to Computational Chemistry")



Spin states in Fe complexes

(Wójcik & co. *Biochemistry* 2012, 51, 9570+
+private comm. with Tomasz Borowski)



	ω_{sym}	ω_{asym}	ω_{bend}
Exp.	1135	1089	716
RHF	1537	1418	867
MP2	1166	2241	743
CCSD(T)	1154	1067	717
LDA/SVWN	1249	1148	744
GGA/BLYP	1130	980	683
hybrid /B3LYP	1252	1194	746

$\Delta E(\text{eV})$ between $S=3$ ($L\text{-Fe}^{3+}\text{-O}\cdot$) & $S=2$ ($L\text{-Fe}^{4+}=\text{O}$)

ROHF	-4.88
CCSD(T)	0.90
B3LYP	0.77

DFT Cooking

❏ Wide choice. Any quantum chemistry code doing HF can do DFT/KS, there are also DFT-only codes with only (semi)local E_{xc} .

❏ http://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid_state_physics_software

- **Molecules** free GAMESS, NWChem, ORCA
commercial Turbomole, Gaussian, ADF, Jaguar
- **Solids** free SIESTA, Quantum Espresso, ABINIT
commercial VASP, Wien2k

❏ Example Gaussian input for H₂O molecule: B3LYP geometry optimization & freq. calc. in STO-3G basis set.

```
# b3lyp/sto-3g opt freq  
  
water  
  
0      1  
O      -0.464      0.177      0.0  
H      -0.464      1.137      0.0  
H       0.441     -0.143      0.0
```

Common DFT Superstitions

- ❑ DFT is empirical, not an *ab initio* method.

(by orthodox quantum chemist)

NOOOO!!! DFT is exact theory (HK theorems)

& KS is in principle exact realization of it.

The issue is that $E_{xc}[\rho]$ is approximated.

Even so, most of current approx. are free of empirical fitting.

Virtually all DFT resentments should be addressed to approx. $E_{xc}[\rho]$.



- ❑ There is no way of systematic improvement of DFT, unlike good ol' quantum chemistry method.

Well, strictly speaking it's right. But there is general scheme how to proceed with improvement of $E_{xc}[\rho]$ (Jacob's ladder).

Common DFT Superstitions

- KS is often OK, but being single determinant method, can't handle strong static correlation. (by moderately liberal quantum chemist)

KS determinant WF is exact WF for fictitious noninteracting reference kohnshamions, having the same ρ as the corresponding system of electrons. If only we knew exact $E_{xc}[\rho]$, KS would give us exact E , even for 'strong static correlation'.

(& in general, for ρ of degenerated state, KS WF can be linear combination of several determinants)

- DFT is ground state theory, can't handle excited states.

In principle, ground state ρ determines full \hat{H} , thus its excited states as well. But because HK2 variational principle holds only for $E_{gs}[\rho]$, practical search for excited states E scheme is somewhat more involved (usually achieved by time dependent DFT)

- DFT can't handle van der Waals interaction.

(Semi)local approx. can't indeed, but nonlocal (even approx.) E_{xc} can.

DFT Common Superstitions

- ❑ KS (spin)orbitals are great! (99.9 % of DFT users)

Practice & certain theoretical considerations justify the use of KS orbitals for interpretative purposes & they are usually better than HF ones. But remember, they are orbitals for kohnshamions, not electrons, use them at your own risk.

- ❑ B3LYP is the best! (by organic chemist).

Nope.

- ❑ If you still experience problems, please consult: J. Perdew "Some Fundamental Issues in Ground State DFT: A Guide For the Perplexed" *J. Chem. Theory Comp.* 2009, 5, 902.

Suggested Reading – Articles & Chapters

- ❏ Chapters about DFT in Jensen, Crammer & Lewars' handbooks.
- ❏ H. Jacobsen & L. Cavallo "Directions for Use of DFT..." in "Handbook of Computational Chemistry", Springer 2012.
- ❏ K. Capelle "A Bird's-Eye View of Density-Functional Theory" *Braz. J. Phys.* 2006, 36, 1318; arxiv.org/pdf/condmat/0211443
- ❏ R. O. Jones "Introduction to DFT & XC Functionals" in NIC Series vol. 31, <http://webarchiv.fz-juelich.de/nic-series//volume31/jones.pdf>
- ❏ W. Kohn, A. D. Becke & R. G. Parr *J. Phys. Chem.* 1996, 100, 12974.
- ❏ J. Perdew & co. *J. Chem. Phys.* 2005, 123, 062201.
- ❏ K. Burke *J. Chem. Phys.* 2012, 136, 150901; K. Burke & L. Wagner *Int. J. Quantum Chem.* 2013, 113, 96.
- ❏ F. Neese *Coord. Chem. Rev.* 2009, 253, 526-563.
- ❏ ... & many, many others.

Suggested Reading – Whole Books

- ❑ W. Koch & M. C. Holthausen "A Chemist's Guide to Density Functional Theory" Wiley 2001.
- ❑ "A Primer in Density Functional Theory" Springer 2003.
- ❑ K. Burke "The ABC of DFT" <http://www.chem.uci.edu/~kieron/dftold2/materials/bookABCDFT/gamma/g1.pdf>
- ❑ J. Kohanoff "Electronic Structure Calculations for Solids & Molecules: Theory & Computational Methods" Cambridge 2006.
- ❑ R. Martin "Electronic Structure: Basic Theory & Practical Methods" Cambridge 2010.
- ❑ & many others ...

THE LAST SLIDE



THANK YOU FOR YOUR ATTENTION!

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Appendix A: N- & v-representability

- ❑ **N-representability question:** does every (physically reasonable) ρ can be obtained from integration of certain N-particle antisymmetric Ψ ?

$$\rho(\mathbf{r}) = N \sum_{\sigma_i} \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3 \dots \mathbf{x}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N$$

YES (Gilbert *PR-B*, 1975, 12, 2111)

- ❑ **v-representability question:** does every (N-representable) ρ can be obtained from Ψ associated with external potential (being eigenfunction of \hat{H} containing v_{ext}).

Well, not proved in general case. Note that this is important for validation of KS method, it assumes the existence of effective v_s for which ρ_s (of nonint. particles) equals to ρ (of real electrons).

Nevertheless, many important special cases of v-representability were proved & it doesn't seem to be big problem in practice.

- ❑ Original HK proofs was given only for v-representable ρ , Lieb & Levy later showed that E can be expressed as functional of ρ for any N-representable ρ .

Appendix B: Tales of Two Correlation Energies

- ❑ In (nonrelativistic) quantum chemistry correlation energy E_c is defined as the difference between exact (full CI in complete basis set) & HF energy (in the same basis set)

$$E_C^{HF} = E_{exact} - E_{HF} = E_{exact} - \langle \Psi_{HF} | \hat{H}_e | \Psi_{HF} \rangle$$

- ❑ In KS, E_c is the difference between total E_{xc} & E_x only, which is

$$E_C^{DFT} = E_{XC} - E_X = E_{exact} - \langle \Psi_{KS} | \hat{H}_e | \Psi_{KS} \rangle$$

- ❑ Because Ψ_{HF} is Slater determinant minimizing $\langle \Psi_{SD} | \hat{H}_e | \Psi_{SD} \rangle$ then

$$E_C^{DFT} \leq E_C^{HF}$$

- ❑ Anyway, remember that DFT with exact $E_{xc}[\rho]$ should give exact total E & this is what really matters!

Appendix C: Exchange-Correlation Hole & Adiabatic Connection

Pair density $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ describes probability density of concurrent finding of 2 el. in \mathbf{r}_1 & \mathbf{r}_2 , respectively: $\rho_2(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \sum_{\sigma_i} \int |\Psi|^2 d\mathbf{r}_3 \dots d\mathbf{r}_N$

XC hole describes difference in 2-body probability density for independent & correlated particles (kohnshamions & electrons)

$$\rho_2^{corr}(\mathbf{r}_1, \mathbf{r}_2) \neq \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) + \rho(\mathbf{r}_1)h_{XC}(\mathbf{r}_1, \mathbf{r}_2)$$

$$\int \int \rho_2^{corr}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = N(N-1), \quad \int \int h_{XC}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = -1$$

Consider \hat{H} dependent on parameter λ , which vary from 0 for KS particle, to 1 for real electrons: $\hat{H}_\lambda = \hat{T} + \lambda \sum_{i,j} r_{ij}^{-1} + \hat{V}_{ext}^\lambda$, where \hat{V}_{ext}^λ gives always the same (real electrons) ρ (i. e. is changed **adiabatically**).

Exact $E_{XC}[\rho]$ can be expressed as the Coulomb interaction between ρ & h_{XC} , averaged over λ : $E_{XC}[\rho] = \int_0^1 d\lambda \int \int \rho(\mathbf{r}_1) h_{XC}(\lambda, \mathbf{r}_1, \mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2$ with the leading contribution $V_{XC}[\rho] = \int \int \rho(\mathbf{r}_1) h_{XC}^{\lambda=1}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2$

It was shown that spherically averaged h_{XC} in LDA & GGA resembles pretty well the accurate one (known for model systems).

Appendix D: Several Certain Conditions & Example E_c Functional

- ▣ (1) Size consistency $R_{AB} \rightarrow \infty \Rightarrow E[\rho_A + \rho_B] = E[\rho_A] + E[\rho_B]$
- ▣ (2) Spin scaling $E[\rho^\alpha, \rho^\beta] = 1/2 (E_X[2\rho^\alpha] + E_X[2\rho^\beta])$
- ▣ (3) Lieb-Oxford lower bound $E_X[\rho] \geq E_{XC}[\rho] \geq 2.273 E_{XC}^{LDA}[\rho]$
- ▣ (4) One electron limit $E_C[\rho_1] = 0 \wedge E_X[\rho] = -J[\rho_1]$
 (removal of spurious self-interaction from Coulomb energy only)
- ▣ Every (semi)local functional fulfills (1) & (2), LDA & several GGA functional (like PBE) satisfy (3). Regarding (4), $E_C[\rho_1] = 0$ is fulfilled by meta-GGA, but to get $E_X[\rho] = -J[\rho_1]$ one needs fully nonlocal (KS orbital dependent) functional.

▣ Perdew-Zunger formula for LDA E_c

$$\varepsilon_C^{PZ} = \begin{cases} A \ln r_s + B + C r_s \ln r_s + D r_s, & r_s \leq 1 \\ \frac{\alpha}{1 + \beta \sqrt{r_s} + \gamma r_s}, & r_s > 1 \end{cases}$$

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

$$E_C^{PZ} = \int \rho(r) \varepsilon_C^{PZ} d\mathbf{r}$$

Appendix E: N-discontinuity of chemical potential

- Derivative of E with respect to no. of el. is discontinuous for integers:

$$\left(\frac{\partial E}{\partial n} \right)_{N+} = E(N-1) - E(N) = I > A = E(N) - E(N+1) = \left(\frac{\partial E}{\partial n} \right)_{N-}$$

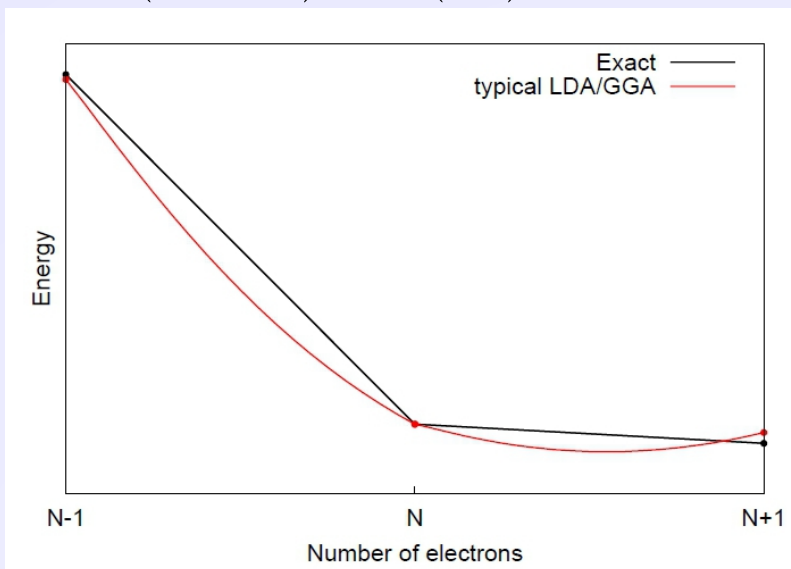


Fig. from Cohen & co. "A fractional view of the XC Functional..."

http://www.psi-k.org/newsletters/News_99/Highlight_99.pdf

- All (semi)local approx. for E_{xc} can't reproduce this feature of exact E .
- Note that: $\left(\frac{\partial T_s}{\partial n} \right)_{N+} = \epsilon_{HOMO}(N) \neq \epsilon_{LUMO}(N) = \left(\frac{\partial T_s}{\partial n} \right)_{N-}$
- Thus even for exact density functional KS HOMO-LUMO gap is not equal to the fundamental gap ($I-A$)! (& optical as well, as this is the difference between $E(N)$ of the 1st excited & ground state).