

Crash Course in The Density Functional Theory

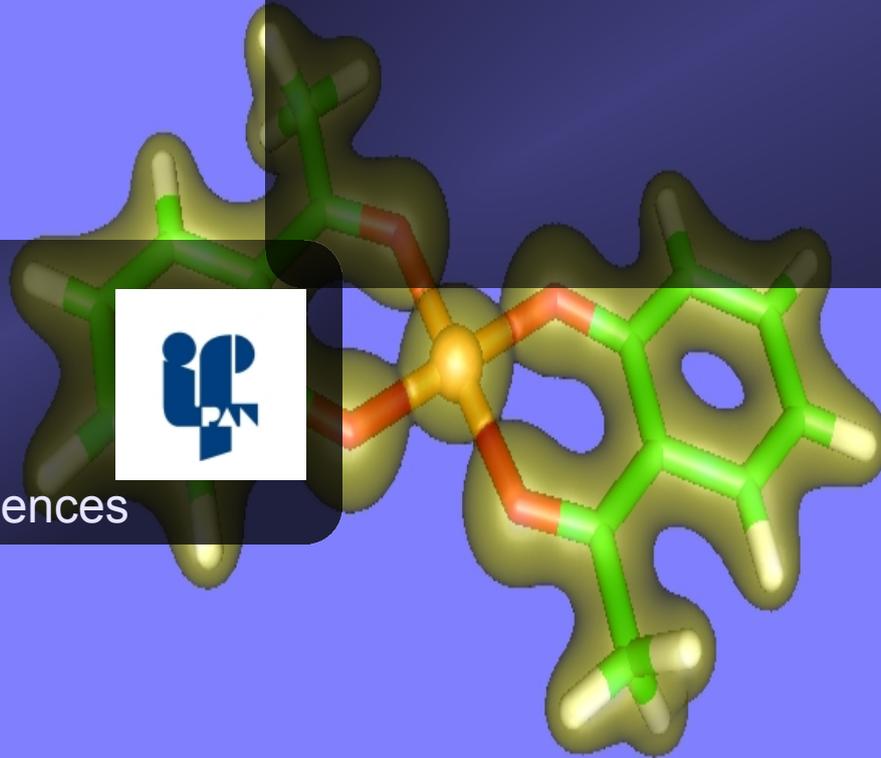
Introduction to Molecular Modeling



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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.
- HF methods delivers 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 (=spin unpolarized) 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)

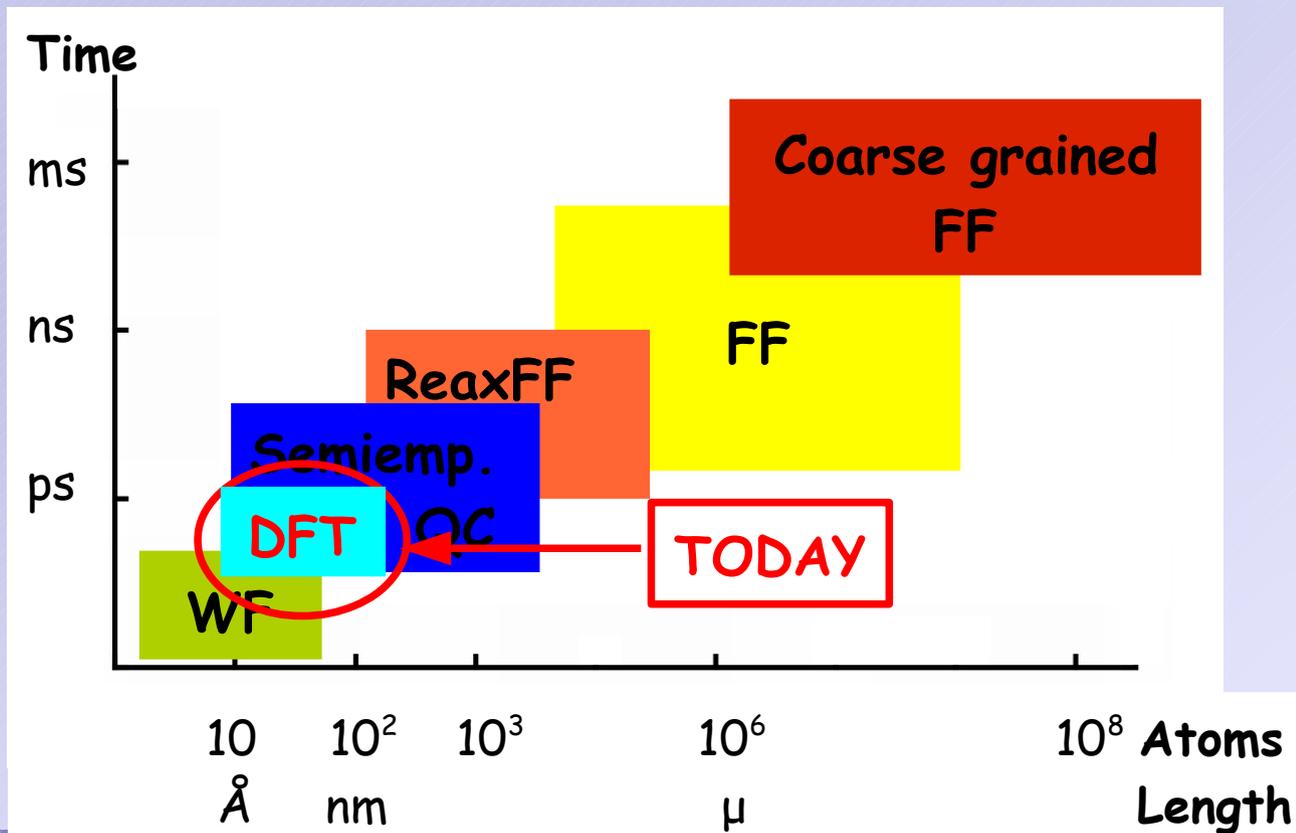
- HF method correctly describes, due to the antisymmetric form of SD, **exchange correlation**, i. e. between el. of the same spin.
- Coulomb correlation** is missing, due to the mean field treatment of e-e interactions.
- Correlation Energy** $E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} < 0$, 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.



- The exact N-el. WF can be represented as a linear combination of many SD → **Configuration Interaction** method. In practice **full CI** can be done for very small molecules (up to 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

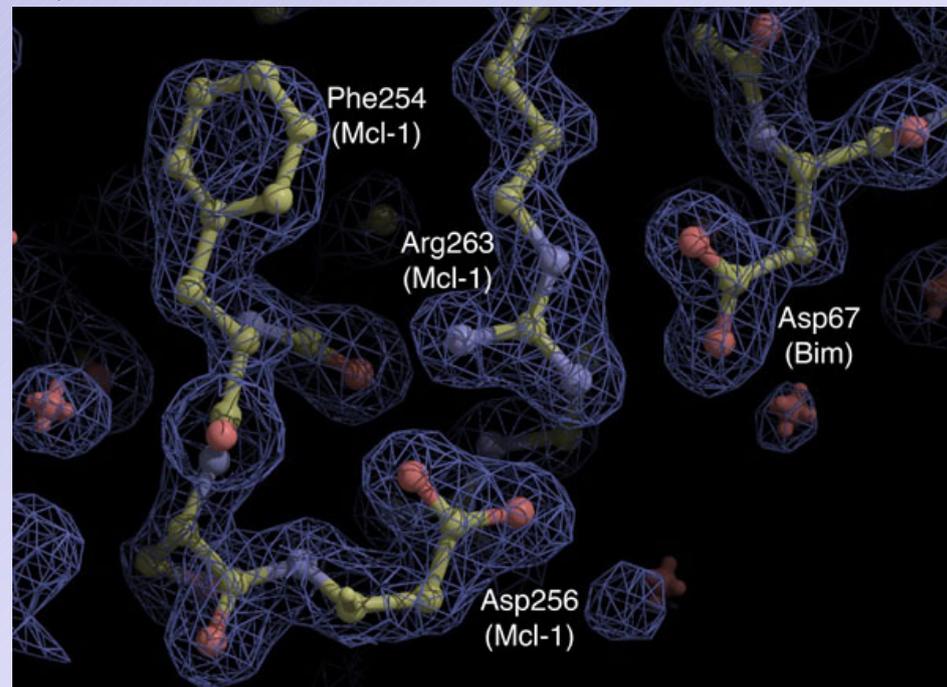
$$\rho(\mathbf{r}) = N \sum_{\sigma_i} \int |\Psi(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3 \dots \mathbf{q}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N, \quad \mathbf{x} = (\mathbf{r}, \sigma)$$

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

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

• $\rho(\mathbf{r})$ 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)

$$E_{TF} = T_{TF} \int \rho(\mathbf{r})^{5/3} d\mathbf{r} + \int v_{ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

interaction with external potential 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} .

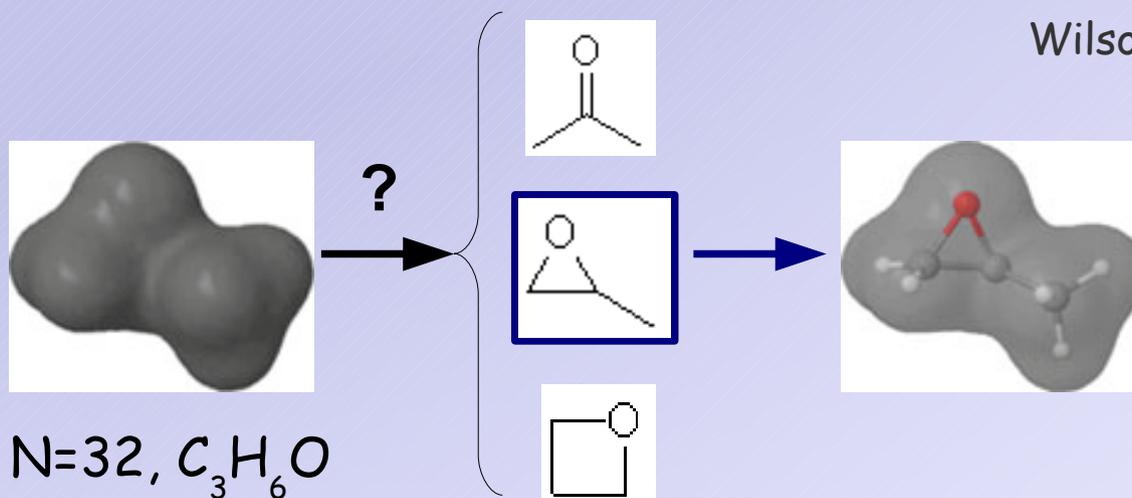


Fig. after Jacobsen & Cavallo "Directions For Use DFT..." in "Handbook of Computational Chemistry Vol. 1" Springer, 2012.

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)

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

- $E_{xc}[\rho]$ 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_I, R_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.

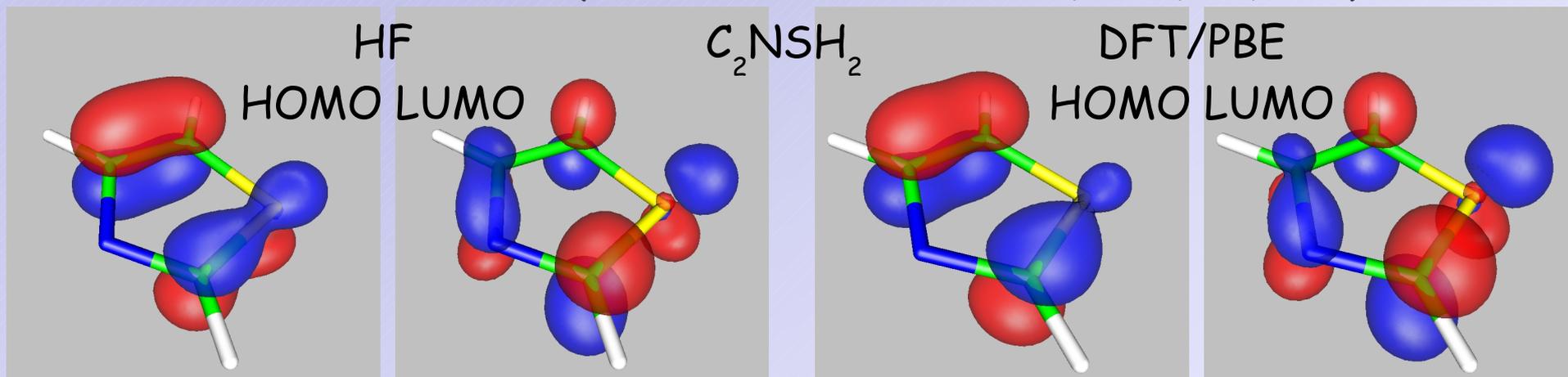
KS Orbitals & Orbital Energies

- 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)

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

- 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?

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

$$T_s[\rho] = \sum_i \left\langle \varphi_i^{KS}(\mathbf{1}) \left| -\left(\frac{1}{2}\right) \nabla_1^2 \right| \varphi_i^{KS}(\mathbf{1}) \right\rangle$$

• 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 $\Delta E \sim 0.01 \text{ eV}$

Heaven of Chemical Accuracy

Exact XC
(+ virtual φ^{KS})

hyper-GGA
(+exact exchange/occ. φ^{KS})

meta-GGA
(+ $\nabla^2\rho$)

Generalized Gradient
Approx. (+ $\nabla\rho$)

Local Density Approx.
(ρ only)

Hartree World

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 $\mathbf{r}+d\mathbf{r}$.

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

- 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. non-electrostatic 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 $E_{xc}[\rho]$ (just like it should be exactly). In practice, 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.

- Majority 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:



- B3LYP hybrid gained huge popularity in (organic) chemistry (in 2007 80% of DFT citations) - but it is not flawless, even for main group elements. (see for example: Grimme *Angew. Chem. Int. Ed.* **2006**, *45*, 4460)
- Hybrid-meta-GGA M06 is gaining popularity in recent years.
- Personal recommendation - if you do not know, which to choose, choose gradient PBE & if it doesn't work choose hybrid PBE0. They are empirical parameters free & they are good (except the cases, where they are bad, of course:].

Making Shortcuts in DFT

- Many solutions to specific DFT problems proposed.
- **Van der Waals interactions:** perhaps the simplest approach to account for them is semiempirical DFT-D scheme

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

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

- Adding nonlocal corr. to (semi)local EXC. This corr. in 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^α, ρ^β only in relativistic case.
- In practice, approx. $E_{xc}[\rho^\alpha, \rho^\beta]$ 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 ($H^\alpha + H^\beta$).

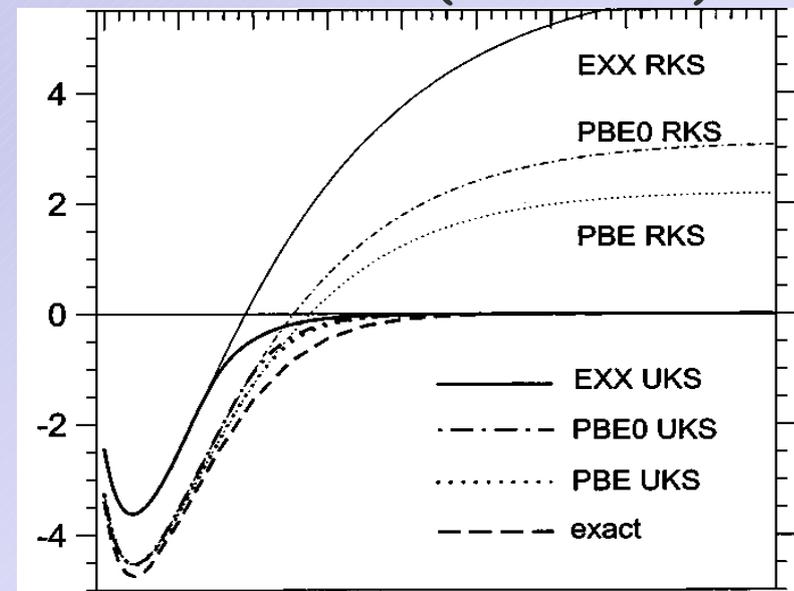


Fig from Fuchs et al. *JCP* 2005, 122, 094116.

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

Why Do We Like DFT (in KS variant)?

- Simply, it is correlated method with computational cost of HF (or less).
- For strongly correlated systems, like transition metals, HF practically always fail, 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

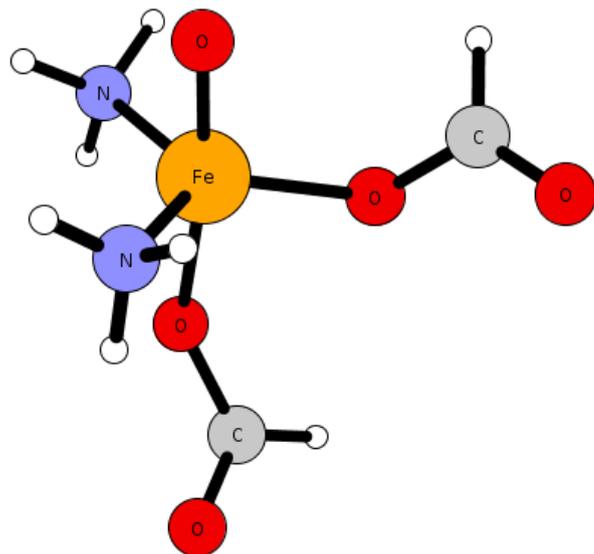
Harmonic O_3 frequencies (Jensen "Introduction to Computational Chemistry")



	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

Spin states in Fe complexes

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



ΔE (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

Common DFT Superstitions

- ❖ DFT is empirical, not an *ab initio* method.
(by orthodox quantum chemist)

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

& KS is in principle exact realization of it.

The issue is that approx. are used for $E_{xc}[\rho]$. Even so, most of current approx. are free of empirical fitting.

In short - 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).

Oh, BTW, why don't you use MP3 over MP2?



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.
- R. F. Nalewajski "Podstawy i Metody Chemii Kwantowej" PWN 2001.
- ... & 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.



THANK YOU FOR YOUR ATTENTION!

(& to prof. Tomasz Borowski for peer-review)

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 (Kohn-Sham ions & 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

$$\varepsilon_C^{PZ} = \begin{cases} A \ln r_s + B + C r_s \ln r_s + D r_s, & r_s \leq 1 \\ \frac{\alpha}{1 + \beta \sqrt{r_s} + \gamma r_s}, & r_s > 1 \end{cases} \quad r_s = \left(\frac{3}{4\pi\rho(r)} \right)^{(1/3)}$$

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

Appendix E: N-discontinuity of chemical potential

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

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

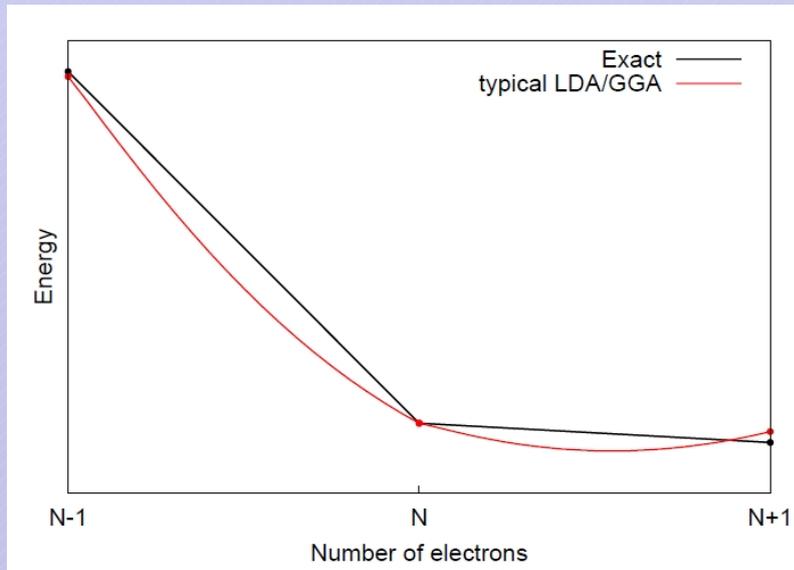


Fig. from Cohen & co. "A fractional view of the XC Functional..."

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).