Hartree-Fock and Density Functional Theory

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Karin Fink WFS-2025 Hartree-Fock and Density Functional Theory

Electronic Schrödinger equation

• Electronic eigenvalue equation (from Jonas talk):

$$\begin{bmatrix} \sum_{i=1}^{N} \left(\frac{-\hbar^2}{2m_e} \nabla_i^2 - \sum_{\alpha=1}^{\nu} \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 |\mathbf{R}_{\alpha} - \mathbf{r}_i|} + \sum_{j>i}^{N} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_j - \mathbf{r}_i|} \right) \\ + \sum_{\alpha=1}^{\nu} \sum_{\beta>\alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi\epsilon_0 |\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|} \end{bmatrix} \Psi_m(\mathbf{r}, \mathbf{R}) = E_m(\mathbf{R}) \Psi_m(\mathbf{r}, \mathbf{R})$$

(nuclear coordinates treated as parameters)

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• Electronic eigenvalue equation in atomic units: $m_e = 1, \hbar = 1, 4\pi\epsilon_0 = 1$ (https://en.wikipedia.org/wiki/Atomic_units]

$$\begin{bmatrix} \sum_{i=1}^{N} \left(\frac{-1}{2} \nabla_{i}^{2} - \sum_{\alpha=1}^{\nu} \frac{Z_{\alpha}}{|\boldsymbol{R}_{\alpha} - \boldsymbol{r}_{i}|} + \sum_{j>i}^{N} \frac{1}{|\boldsymbol{r}_{j} - \boldsymbol{r}_{i}|} \right) \\ + \sum_{\alpha=1}^{\nu} \sum_{\beta>\alpha}^{M} \frac{Z_{\alpha} Z_{\beta}}{|\boldsymbol{R}_{\alpha} - \boldsymbol{R}_{\beta}|} \end{bmatrix} \Psi_{m}(\boldsymbol{r}, \boldsymbol{R}) = E_{m}(\boldsymbol{R}) \Psi_{m}(\boldsymbol{r}, \boldsymbol{R}),$$

Hartree-Fock theory: many-electron wave function

- Electrons are indistiguishable, exchanging all coordinates of two electrons does not change $\Psi^*\Psi$
- Electrons are fermions (spin 1/2 particles) Permutation property of wavefunction (density)

$$\Psi(1,2,..,n,..,m,..,N) = -\Psi(1,2,..,m,..,n,..,N)$$

- Wave function depends on spatial r_i and spin ω_i coordinates of all electrons i denoted as x_i
- Spin functions are either $\sigma(\omega_i) = \alpha$ for $m_s = \frac{1}{2}$ or $\sigma(\omega_i) = \beta$ for $m_s = -\frac{1}{2}$
- $\hat{s}_z lpha = rac{1}{2} lpha$ and $\hat{s}_z eta = -rac{1}{2} eta$
- Spin integration $<\alpha|\alpha>=$ 1, $<\beta|\beta>=$ 1, $<\alpha|\beta>=$ 0, $<\beta|\alpha>=$ 0

Hartree-Fock theory: Slater determinant

 Hartree product: simplest approach for the many-electron wave function: Product of one-electron wave-functions (orbitals) φ_i(x_i) = ψ_i(r_i)σ_i(ω_i)

$$\Psi(1,2,..,N) = \varphi_1(x_1)\varphi_2(x_2)..\varphi_n(x_n)$$

• Slater determinant: antisymmetrized

$$\Psi(1, 2, .., N) = \Phi = \frac{1}{\sqrt{N!}} \det \begin{vmatrix} \varphi_1(x_1) & \varphi_2(x_1) & .. & \varphi_n(x_1) \\ \varphi_1(x_2) & \varphi_2(x_2) & .. & \varphi_n(x_2) \\ .. & .. & .. \\ \varphi_1(x_n) & \varphi_2(x_n) & .. & \varphi_n(x_n) \end{vmatrix}$$

Hartree-Fock theory: Energy of a Slater determinant

- $\varphi_i(x_i)$ are normalized and orthogonal
- Energy expectation value

$$E_{\Phi} = <\Phi \left| \hat{H}
ight| \Phi >$$

Hamiltonian

$$\hat{\mathcal{H}} = \hat{h}_0 + \sum_i \hat{h_i} + \sum_{i < j} \hat{g_{ij}}$$

- Nuclear repulsion energy $\langle \Phi | \hat{h}_0 | \Phi \rangle = \sum_{\beta > \alpha}^M \frac{Z_{\alpha} Z_{\beta}}{|R_{\alpha} R_{\beta}|}$
- One-electron contributions: kinetic energy + electron-nuclei attraction

$$<\Phi \left| \hat{h}_1 \right| \Phi > = \sum_{i=1}^{N} < arphi_i \left| \left(-rac{1}{2}
abla_i^2 - \sum_{lpha=1}^{
u} rac{Z_lpha}{\left| oldsymbol{R}_lpha - oldsymbol{r}_i
ight|
ight) arphi_i >$$

Continued \hat{g}_{ij}

• Two-electron contribution

$$E_{(2)} = \left\langle \Phi \left| \sum_{i < j} \frac{1}{r_{ij}} \right| \Phi \right\rangle = \frac{1}{2} \sum_{i,j} \left\langle \varphi_i \left| \hat{J}_j - \hat{K}_j \right| \varphi_i \right\rangle = \frac{1}{2} \sum_i \left\langle \varphi_i \left| \hat{J} - \hat{K} \right| \varphi_i \right\rangle$$

with

$$\langle \varphi_i | \hat{J}_j - \hat{K}_j | \varphi_i
angle = \int \varphi_i^*(i) \varphi_j^*(j) \; rac{1}{r_{ij}} \, arphi_i(i) arphi_j(j) \, d au_i d au_j - \int \varphi_i^*(i) arphi_j^*(j) \; rac{1}{r_{ij}} \, arphi_j(i) arphi_i(j) \, d au_i d au_j$$

if [ab|cd] denotes the integral

$$[ab|cd] = \left\langle \varphi_{a}\varphi_{b} \left| \frac{1}{r_{ij}} \right| \varphi_{c}\varphi_{d} \right\rangle = \int \varphi_{a}^{*}(i)\varphi_{b}^{*}(j) \frac{1}{r_{ij}} \varphi_{c}(i)\varphi_{d}(j) d\tau_{i}d\tau_{j}$$

$$E_{(2)} = \sum_{i < j} \{ [ij|ij] - [ij|ji] \}$$

note the case i = j we will come back to it many times..

Hartree-Fock: Variational principle

- How can we determine the orbitals φ_i
- Minimize energy expectation values by varying the form of the orbitals
- For optimized orbitals, the energy remains constant for small changes of the orbitals E[Φ + δΦ] E[Φ] = 0
- Fock equations (effective one-electron equtions)

$$\hat{f} arphi_i = \left(\hat{h}_1 + \sum_j [\hat{J}_j - \hat{K}_j]
ight) arphi_i = \epsilon_i arphi_i$$

- Self consistent field approach
- In practice most popular way: use a set of basis functions for the orbitals φ_i

• Orbitals are expressed as a linear combination of basis functions χ_{μ}

$$arphi_i = \sigma_i \sum_{\mu} c_{i\mu} \chi_{\mu}$$

- $c_{i\mu}$ are the orbital expansion coefficients of orbital φ_i
- Choice of basis functions: see tomorrows lecture by Valera Linear combinations of Gaussian type orbitals for molecules Plane waves for solids

Roothaan-Hall equations

• take Fock equation and replace φ_i by $\sigma_i \sum_{\mu} c_{i\mu} \chi_{\mu}$

$$\hat{f}\varphi_{i} = \hat{f}\sigma_{i}\sum_{\mu}c_{i\mu}\chi_{\mu} = \left(\hat{h}_{1} + \sum_{j}\left[\hat{J}_{j} - \hat{K}_{j}\right]\right)\sigma_{i}\sum_{\mu}c_{i\mu}\chi_{\mu} = \epsilon_{i}\sigma_{i}\sum_{\mu}c_{i\mu}\chi_{\mu}$$

• multiply from the left with $\sigma_i \chi^*_{\nu}$ and integrate

$$\sum_{\mu} c_{i\mu} \langle \chi_{\nu} | \hat{f} | \chi_{\mu} \rangle = \epsilon_{i} \sum_{\mu} c_{i\mu} \langle \chi_{\nu} | \chi_{\mu} \rangle$$

Matrix elements $F_{
u\mu} = \langle \chi_{
u} \, | \, \hat{f} | \, \chi_{\mu}
angle$ and $S_{
u\mu} = \langle \chi_{
u} \, | \, \chi_{\mu}
angle$

• Matrix equation $\mathbf{FC} = E\mathbf{SC}$

Roothaan-Hall equations: continued

$$F_{\nu\mu} = \left\langle \chi_{\nu} \left| \hat{h}_{1} \right| \chi_{\mu} \right\rangle + \left\langle \chi_{\nu} \left| \sum_{j} \left[\hat{J}_{j} - \hat{K}_{j} \right] \right) \right| \chi_{\mu} \right\rangle$$

• $\sum_{j} \hat{J}_{j} - \hat{K}_{j}$ depends on orbitals and molecular orbital coefficients C• Iterative procedure: Self consistent field (SCF) cycles

Solve *FC* = *ESC* and obtain *C* Construct new *F* from *C* and so on

Spin integration for Coulomb J and exchange operator K

 $\bullet\,$ Fock-operator depends on spin functions, assume F is applied on an α spinorbital

$$\begin{aligned} F^{\alpha}_{\nu\mu} &= \langle \chi_{\nu} | \hat{h}_{1} | \chi_{\mu} \rangle < \alpha | \alpha > \\ &+ \sum_{\rho\sigma} \sum_{j} c_{j\rho} c_{j\sigma} (\langle \chi_{\nu}(1) \alpha(1) \chi_{\rho}(2) \sigma_{j}(2) | \chi_{\mu}(1) \alpha(1) \chi_{\sigma}(2) \sigma_{j}(2) \rangle \\ &- \langle \chi_{\nu}(1) \alpha(1) \chi_{\rho}(2) \sigma_{j}(2) | \chi_{\sigma}(1) \sigma_{j}(1) \chi_{\mu}(2) \alpha(2) \rangle) \end{aligned}$$
(1)

• If the second electron has β spin, the exchange integral vanishes. Exchange reduces the Coulomb repulsion for electrons with the same spin.

$$\mathcal{F}^{\alpha}_{\nu\mu} = \langle \chi_{\nu} | \hat{h}_{1} | \chi_{\mu} \rangle + \sum_{\rho\sigma} \left(D_{\rho\sigma} \langle \chi_{\nu}(1)\chi_{\rho}(2) | \chi_{\mu}(1)\chi_{\sigma}(2) \rangle - D^{\alpha}_{\rho\sigma} \langle \chi_{\nu}(1)\chi_{\rho}(2) | \chi_{\sigma}(1)\chi_{\mu}(2) \rangle \right)$$

• Total density
$$D_{
ho\sigma} = \sum_j c_{j
ho} c_{j\sigma}$$

•
$$lpha$$
-Density $D^{lpha}_{
ho\sigma} = \sum_j c_{j
ho} c_{j\sigma} \delta_{lpha\sigma_j}$ and eta -Density $D^{eta}_{
ho\sigma} = \sum_j c_{j
ho} c_{j\sigma} \delta_{eta\sigma_j}$

• Spin density
$$D^{SD}=D^lpha-D^eta$$

Different types of Hartree-Fock

• Unrestricted Hartree-Fock

Construct F^{α} and F^{β} and solve the Fock-equations independently.

- Restricted Hartree-Fock for closed shell systems There are pairs of α - and β -orbitals with the identical spatial function $\psi(r)$. (Restriction) $D^{\alpha} = D^{\beta} = \frac{1}{2}D$ $F^{\alpha} = F^{\beta}$
- Restricted open-shell Hartree-Fock

Different combinations of Fock-operators (constructed with D and $D^{\alpha-\beta}$ in the space of the kanonical Hartree-Fock orbitals.

Important for half filled shells, triplet states, open shell singlet states Alternative: CASSCF (more flexible and easier to handle) Electronic wavefunctions are very complicated

- Coupled Cluster Ansatz is required for high accuracy
- High flexibility needed for electronic wave functions (nuclear-electron and electron-electron cusps)
- Unfavourable scaling with system size

However, only the one particle density can be observed

$$\rho(\vec{r}) = n \int \Psi^*(\vec{r}, \vec{r_2}, \dots, \vec{r_n}) \Psi(\vec{r}, \vec{r_2}, \dots, \vec{r_n}) \mathrm{d}\vec{r_2} \dots \mathrm{d}\vec{r_n}$$

(Motivation: expectation value of multiplicative 1e operators)

Determine electronic properties from the density only (!?)

P. Hohenberg and W. Kohn, Phys. Rev. B 136, (1964) 864-871

Theorem

The external potential is a unique functional of the ground state density (apart from a trivial additive constant).

Theorem

For a given external potential v_{ext} there exists only a single ground state density ρ . Both determine each other uniquely.

 $v_{ext} \Leftrightarrow \rho$

Theorem

There is a functional of the density that becomes minimal for the exact ground state density with the value of the exact ground state energy

The normalized ground state wavefunction $\boldsymbol{\Psi}$ is a unique function of the density and the external potential

$$\Psi = \Psi[v_{ext}] = \Psi[
ho]$$

⇒ ground state energy $E_0 = E[\rho] = E[v_{ext}]$ Ritz variational principle ⇒

$$\begin{split} E_{0} &= E[\rho] = \langle \Psi | \, \hat{T} + v_{ext} + \hat{V}_{ee} + V_{nn} | \Psi \rangle \\ &= \underbrace{\langle \Psi | \, \hat{T} | \Psi \rangle}_{\mathcal{T}[\rho]} + \int \rho(\vec{r}) \, v_{ext}(\vec{r}) \, \mathrm{d}\vec{r} + V_{ee}[\rho] + V_{nn} \end{split}$$

Bright Wilson's observation

From the exact electron density ρ we may obtain

- Electron number $n = \int \rho(\vec{r}) \, \mathrm{d}\vec{r}$
- Nuclear positions R_I : cusps of the density
- Nuclear charges $Z_I \lim_{r \to R_I} \left(\frac{\partial \rho}{\partial \vec{r}} \right) = -2 Z_I \rho$
- $\Rightarrow \rho$ determines \hat{H}
- $\Rightarrow \Psi$ and *E* are available via $\hat{H}\Psi = E\Psi$

 $\Rightarrow
ho$ can be determined from Ψ



Contributions to the electronic energy

As a rule the correct wavefunction $\Psi \approx \Phi_0$ (HF)-Slater determinant

correlation Energy contributions to the exact energy

$$egin{aligned} \langle E
angle_{\Psi} &= \langle \Phi_0 | \hat{H} | \Phi_0
angle + \langle \Phi_0 | \hat{H} | \Psi_c
angle \ &= \mathcal{T} + \int
ho(\vec{r}) \, \mathbf{v}_{ext} \, \, \mathrm{d}\vec{r} + 2J - \mathcal{K} + \mathcal{E}_c \end{aligned}$$

T kinetic energy

 $\Rightarrow \Psi = \Phi_0 + \Psi_c$

J Coulomb energy $J = 2 \sum_{i,j=1}^{n/2} \langle \psi_i \psi_j | \psi_i \psi_j \rangle = \frac{1}{2} \iint \frac{\rho(\vec{r_1})\rho(\vec{r_2})}{r_{12}} \, \mathrm{d}\vec{r_1} \, \mathrm{d}\vec{r_2}$ Functional of the density

$$E_{x}$$
 Exchange energy $E_{x}=-K=\sum_{i,j=1}^{n/2}\langle\psi_{i}\psi_{j}|\psi_{j}\psi_{i}
angle$

 E_c correlation energy E_c

Contributions to total electronic energies

Energy as functional of ρ

$$E[\rho] = T[\rho] + \int v_{ext}(\vec{r})\rho(\vec{r}) \,\mathrm{d}\vec{r} + V_{ee}[\rho] + V_{nn}$$

$$V_{ee}[\rho] = \underbrace{\frac{1}{2} \int \frac{\rho(\vec{r_1})\rho(\vec{r_2})}{r_{12}} \mathrm{d}\vec{r_1} \mathrm{d}\vec{r_2}}_{J[\rho]} + \underbrace{E_x[\rho]}_{\mathsf{Exchange}} + \underbrace{E_c[\rho]}_{\mathsf{Correlation}}$$

Problem: size of contributions

Neon energy contribution	value (E_{h})	(kcal/mol)
T	128.9	81500
J	97.3	61000
E_x	-12.1	-7600
E_c	-0.4	-250

Jellium model (homogeneous electron gas)

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- Jellium (from jelly homogeneous/uniform jam)
- n e[−] in cube edge length *I*, volume V = I³ ⇒ ρ = n/V homogeneous positive background ⇒ neutral system

$$E[\rho] = T[\rho] + \int \rho(\vec{r}) v_{ext}(\vec{r}) d\vec{r} + V_{ee}[\rho] + V_{nn}$$
$$= T[\rho] + \underbrace{J[\rho] + \int \rho(\vec{r}) v_{ext} d\vec{r} + V_{nn}}_{0} + E_x + E_c$$

• orbitals:
$$\psi_{\vec{k}} = \frac{1}{\sqrt{I^3}} e^{i \vec{k} \cdot \vec{r}}$$
 wavefunction: $\Phi = \left| \left| \prod_{\vec{n}} \psi_{\vec{k}} \overline{\psi}_{\vec{k}} \right| \right|$
with $\vec{k} = \frac{2\pi}{I} \vec{n}$; $n_x, n_y, n_z = 0, \pm 1, \pm 2, \dots$

- Fermi-energy $E_F = \frac{(3\pi^2)^{2/3}}{2}\rho^{2/3}$ "highest occupied energy level"
- Thomas-Fermi energy $\mathcal{T}[\rho] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{5/2}(\vec{r}) \,\mathrm{d}\vec{r}$ Kinetic energy functional
- Dirac, Bloch, Slater exchange $E_x = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3} d\vec{r}$ Exchange functional

- In the second second
- 2 Accuracy of orbital free DFT

Energy contributions for Neon in

	Ε	exact	Jellium model	method
$E_h(kcal/mol)$	Т	128.9 (81500)	115 (72000)	Thomas-Fermi
	E_x	-12.1(-7600)	-10.9(-6900)	Slater-exchange

Kohn-Sham determinant and kinetic energy

Walter Kohn and Lu Jeu Sham, Phys. Rev. A, 140, 1133 (1965) set:

$$\rho(\vec{r}) = \rho[\Phi_{KS}] = \rho[||\phi_1\phi_2\dots\phi_n||]$$
$$= \sum_{i=1}^n |\phi_i(\vec{r})|^2$$

Kinetic energy is mostly: $T_s[\vec{\phi}] = \sum_i \langle \phi_i | -\frac{1}{2}\Delta | \phi_i \rangle$

Idea Kohn-Sham DFT:

Employ orbitals $\phi_1, \phi_2 \dots \phi_n$ to

() generate a proper density $\rho(\vec{r}) = \sum_{i=1}^{n} \int \phi_i^*(\vec{r}, \sigma) \phi_i(\vec{r}, \sigma) d\sigma$

2 calculate major part of the kinetic energy (T_s)

Exchange correlation functional

Electrons avoid each other \Rightarrow additional kinetic energy Energy functional

$$E_{\text{KS-DFT}}[\rho] = T_s[\vec{\phi}] + \int v_{ext}(\vec{r}) \rho(\vec{r}) \, \mathrm{d}\vec{r} + \underbrace{\frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2}_{J[\rho]} + E_{xc}[\rho]$$

Exchange correlation energy functional

$$E_{xc}[\rho] = T[\rho] - T_s[\vec{\phi}] + E_{ee}[\rho] - J[\rho]$$

As Hartree-Fock: Calculate $\frac{\delta \langle E \rangle_{HF}}{\delta \phi_i}$ for normalized orbitals Hartree-Fock $\left(-\frac{1}{2}\Delta + v_{ext} + J - K\right)\phi_i = \epsilon_i\phi_i$ KS-DFT $\left(-\frac{1}{2}\Delta + v_{ext} + J + \epsilon_{xc}\right)\phi_i = \epsilon_i\phi_i$ with $E_{xc}[\rho] = \int \epsilon_{xc}[\rho]\rho\,\mathrm{d}\vec{r}$ or $\epsilon_{xc}(\vec{r}) = \left(\frac{\delta E_{xc}[\rho]}{\delta\rho}\right)_{\vec{r}}$ E_{xc} Exchange-Correlation energy functional ϵ_{xc} Exchange-correlation potential

LDA Local density approximation: $\epsilon_{xc} = f[\rho(\vec{r})]$ GGA Generalized gradiant approx. $\epsilon_{xc} = f[\rho(\vec{r}), \vec{\nabla}\rho(\vec{r})]$ meta GGA $\epsilon_{xc} = f[\rho, \vec{\nabla}\rho, \nabla^2\rho, \tau(\vec{r})]; \tau(\vec{r}) = \frac{1}{2} \sum_i |\vec{\nabla}\phi_i|^2$ hybrid-functionals $\epsilon_{xc} = f[\rho, \vec{\nabla}\rho, \ldots] - c K$ Double hybrid functionals $E_{xc} = c_1 E_x + (1 - c_2) E_c + c_2 E_{MP2}$ **RPA** Random phase approximation DFT-D Dispersion correction $E_{xc} = E_{xc}(DFT) + E_{ydW}$ Individual exchange and correlation potentials

Local density approximation (LDA) Exchange

Dirac (Slater) Exchange (uniform electron gas)

$$\begin{split} E_x^{\text{Dirac}} &= -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3} \, \mathrm{d}\vec{r} \\ \epsilon_x^{\text{Dirac}} &= -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3} \end{split}$$

Local density approximation (LDA) Correlation

Korrelation: Vosko, Wilk, Nusair, Can. J. Phys., **58**, 1200, (1980). Fit to asymptotic limits and accurate calculations

$$\epsilon_{c}^{VWN} = \frac{A}{2} \left\{ \ln \frac{x^{2}}{X(x)} + \frac{2b}{Q} \tan^{-1} \left(\frac{Q}{2x+b} \right) - \frac{bx_{0}}{X(x_{0})} \left[\ln \frac{(x-x_{0})^{2}}{X(x)} + \frac{2(b+2x_{0})}{Q} \tan^{-1} \left(\frac{Q}{2x+b} \right) \right] \right\}$$

with
$$x = \sqrt[6]{\frac{3}{4\pi\rho}}$$
; $X(x) = x^2 + bx + c$; $Q = \sqrt{4c - b^2}$
 $A = 0.0621814$; $x_0 = -0.409286$; $b = 13.0720$; $c = 42.7198$

Common functionals

- B-LYP Becke 1988 (B88) exchange and Lee-Yang Perdew correlation
- B-P86 B88 exchange and Perdew 1986 (P86) correlation [J. P. Perdew, Phys. Rev. B, 33 (1986) 8822-24]
 - PBE Perdew Burke Ernzerhof exchange and correlation [J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett., 77 (1996) 3865-68.]
 Derivation for free Electron gas and Helium correlation with correct limiting conditions

General Form

$$E_{xc} = \int F[\rho_{\sigma}, \vec{\nabla} \rho_{\sigma} \cdot \vec{\nabla} \rho_{\sigma'}]$$

meta-GGA

Next level of improvement for parameters from the density

- second derivative of the density (Laplacian of ρ)
- Kinetic energy density of the orbitals

$$au(ec{r}) = rac{1}{2} \sum_i |
abla \phi_i(ec{r})|^2.$$

Typical functionals

- Becke 95 contains τ in the correlation potential \Rightarrow less self interaction errors (correct for H-atom) [A. D. Becke, J. Chem. Phys. **98**, 1372 (1996)]
 - VSXC Voorhuis-Scuseria eXchange-Correlation 21 fitted parameters [JCP 109, 400 (1998)].
 - TPSS non-empirical improvement of PBE [Tao, Perdew, Staroverov, Scuseria Phys. Rev. Lett. 82, 146401 (2003)]

Hybrid functionals

basic idea: "'Adiabatic Connection Functionals"' Exchange correlation functional $V_{xc}(\lambda)$ $\lambda = 0$: noninteracting reference (exact exchange) $\lambda = 1$: actual system λ turns on exact $e^- - e^-$ interaction then

$$egin{aligned} \mathcal{E}_{xc} &= \int_{0}^{1} \langle \Psi_{\lambda} | V_{xc}(\lambda) | \Psi_{\lambda}
angle \mathrm{d}\lambda \ &pprox rac{1}{2} \left[\langle \Psi_{0} | V_{xc}(0) | \Psi_{0}
angle + \langle \Psi_{1} | V_{xc}(1) | \Psi_{1}
angle
ight] \end{aligned}$$

substituting the $\lambda=1$ result by LDA, we get

$$E_{xc} \approx \frac{1}{2} \left[E_x^{\text{exact}} + E_x^{\text{LDA}} + E_c^{\text{LDA}} \right]$$

Naming: Hartree-Fock exchange is "'exact"' (admixture helps)

$$E_{xc} = (1 - a) E_x^{GGA} + a E_x^{HF} + E_c^{GGA}$$
1st proposal: $E_{xc}^{B3PW91} = (1 - a) E_x^{LDA} + a E_x^{HF} + b \Delta E_x^{B88} + c \Delta E_c^{PW91}$

with $E_x^{\text{HF}} = K$ Exchange operator also "exact" exchange and a = 0.20, b = 0.72, c = 0.81 fit to atomization energies [A. D. Becke, J. Chem. Phys., **98**, 11623 (1993)] Best known example: B3-LYP

$$E_{xc}^{\mathrm{B3LYP}} = (1-a) E_x^{\mathrm{LDA}} + a E_x^{\mathrm{HF}} + b \Delta E_x^{\mathrm{B88}} + (1-c) E_c^{\mathrm{LDA}} + c E_c^{\mathrm{LYP}}$$

Stephens, Delvin, Chabalowski, Frisch, J. Phys. Chem. 98, 11623 (1994).

B3LYP very frequently used and generally rather reliable. BHLYP also Becke-Half-and-Half-LYP

$$E_{xc} = 0.5 \, E_x^{
m HF} + 0.5 \, E_x^{
m B88} + E_c^{
m LYP}$$

- PBE0 also PBE1PBE a = 0.25 from theoretical considerations [Ernzerhof and Scuseria, J. Chem. Phys. **110**, 5029 (1999)]
- TPSSh 10% exact exchange (a = 0.1) TPSS authors, J. Chem. Phys. 121, 11507 (2004).
 - M06 27% exact exchange. Many parameters. Intended for main group and transition metal thermochemistry [Y. Zhao and D.G. Truhlar, Theor Chem Acc. 120, 215 (2006)]

Double hybride functionals

Combine MP2 with DFT. Part of the correlation is obtained by MP2-like-approach with DFT orbitals and orbital energies. First example: B2-PLYP [S. Grimme, J. Chem. Phys. **124**, 034108 (2006)] Functional (mixture)

$$E^{\text{B2-PLYP}} = (1 - a_x) E_x^{\text{B88}} + a_x E_x^{\text{HF}} + (1 - c) E_c^{\text{LYP}} + c E_c^{\text{MP2}}$$

 $a_x = 0.53, c = 0.27$

$$E_{c}^{\mathrm{MP2}} = -\sum_{ij,ab} \frac{\left(\langle \phi_{a}\phi_{b} | \phi_{i}\phi_{j} \rangle - \langle \phi_{a}\phi_{b} | \phi_{j}\phi_{i} \rangle\right)^{2}}{\epsilon_{a} + \epsilon_{b} + \epsilon_{i} + \epsilon_{j}} \qquad \qquad ij \in \mathrm{occ.}, ab \in \mathrm{virt.}$$

MP2 energy formula. Notable methods: B2-PLYP (first), DSD-BLYP, DSD-PBEP86 (spin-component scaling+dispersion)

- In HF, an electron does not interact with itself, because Coulomb and Exchange contributions J_{ii} =< i|J_i|i>= [ii|ii] = K_{ii} cancel exactly.
- In DFT, J is calculated from the orbitals, K is a functional of the density, the cancellation is not exact.
- The error is smaller for Hybrids
- Very important for very local orbitals, 3d or 4f
- Cheaper solution (in solids): DFT+U

DFT and HF: Orbital energies

- 'HF' potential: One-electron Energy depends on the occupation
- Occupied orbitals interact with N-1 orbitals, virtual orbitals with N
- HF: Koopmans' theorem (for IP and EA) Assumption: The orbitals do not change! $\epsilon_i = \langle i|F|i \rangle = h_{ii} + k \langle ii||kk \rangle$ $E_{n-1} - E_n = -\epsilon_i$ Electron removed from orbital i

Electron removed from orbital i.

- Virtual orbitals feel the repulsion of N electrons. Anions are very often not stable.
- In contrary to local LDA potential: same potential for all orbitals Here, orbital energies work better as approximation for excitation energies.

- 1. HF is a nice theory to understand a molecular system
- 2. It has [intrinsic] limitations, so do not expect to much
- 3. HF is a good starting point for post-HF methods (Coupled cluster, perturbation theory)
- 4. DFT can show good agreement with experiment (but: not systematically improvable)
- 5. DFT depends on the functional