Approximate functionals in DFT and 1RDM-FT

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Exact DFT functionals

Pure state functional (Levy)

$$W_{\mathrm{L}}[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle$$

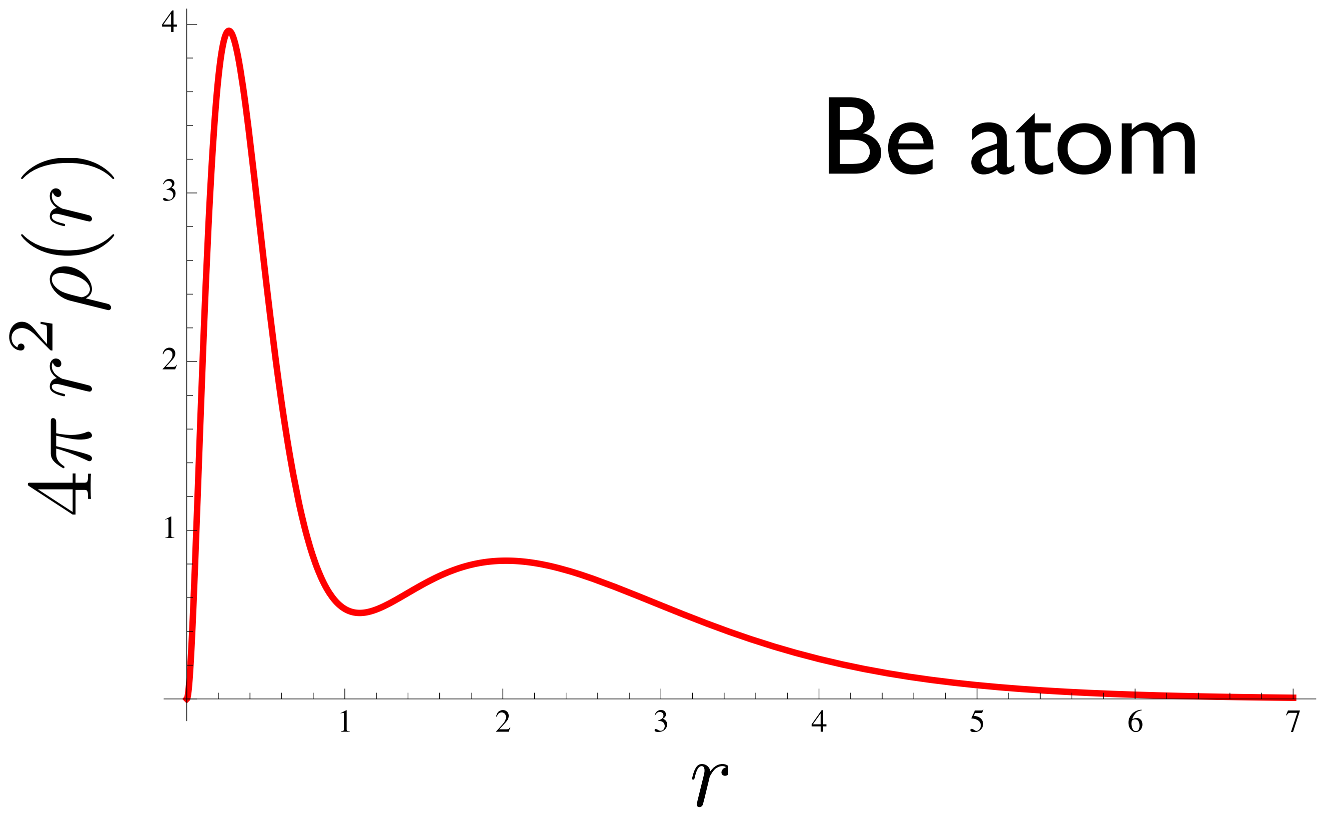
Mixed state functional (Valone/Lieb)

$$W_{\mathrm{V}}[n] = \min_{\hat{\rho} \to n} \mathrm{Tr}\big\{ \hat{\rho} \big(\hat{T} + \hat{W} \big) \big\}$$

$$\mathrm{Tr}\{\cdot\} = \sum_K \langle \Psi_K | \cdot | \Psi_K \rangle \qquad \hat{\rho} = \sum_K w_K |\Psi_K\rangle\langle\Psi_K|$$

weights: $\sum_K w_K = 1$ $\quad 0 \leq w_K (\leq 1)$

Kinetic energy



Impossible (so far) with a kinetic energy functional of the density alone

No success to bind molecules

Kohn–Sham system (1965)

Direct approximation of $T[\rho]$ problematic

non-interacting electrons can describe shell-structure and molecular bonding

$$E[\rho] = T[\rho] + V[\rho] + W[\rho]$$

Approximate by $T_s[\rho]$

Approximate by $W_{\mathrm{H}}[\rho]$

$$W_{\mathrm{H}}[\rho] = \frac{1}{2}\int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 \, \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Kohn–Sham system

$$E[\rho] = T_s[\rho] + V[\rho] + W_{\mathrm{H}}[\rho] + E_{\mathrm{xc}}[\rho]$$

exchange-correlation energy:

$$E_{\mathrm{xc}}[\rho] = \big(T[\rho] - T_s[\rho]\big) + \big(W[\rho] - W_{\mathrm{H}}[\rho]\big)$$

$$T_{\mathrm{c}}[\rho] = T[\rho] - T_s[\rho] \qquad W_{\mathrm{xc}}[\rho] = W[\rho] - W_{\mathrm{H}}[\rho]$$

E_{xc}: stupidity energy (Feynman)

Kohn-Sham system

Universal functional of non-interacting system

$$T_s[\rho] = \min_{\Phi \to \rho} \langle \Phi | \hat{T} | \Phi \rangle = \min_{\gamma \to \rho} T[\gamma]$$

We expect Slater determinant as solution

[though constraint can (and will) mess up: CH_2 and C_2]

$$\left(-\frac{1}{2} \nabla^2 + v_s[\rho](\mathbf{r}) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_i n_i |\phi_i(\mathbf{r})|^2$$

Kohn–Sham potential

$$F[\rho] = E\big[v[\rho] - \mu\big] - \int \mathrm{d}\mathbf{r}\, \big(v[\rho](\mathbf{r}) - \mu\big)\rho(\mathbf{r})$$

exact: $$\frac{\delta E}{\delta v(\mathbf{r})} = \rho(\mathbf{r}) \longrightarrow \frac{\delta F}{\delta \rho(\mathbf{r})} = -v(\mathbf{r}) + \mu$$

KS: $$\frac{\delta E_s}{\delta v_s(\mathbf{r})} = \rho(\mathbf{r}) \longrightarrow \frac{\delta T_s}{\delta \rho(\mathbf{r})} = -v_s(\mathbf{r}) + \mu_s$$

$$F[\rho] = T_s[\rho] + W_{\mathrm{H}}[\rho] + E_{\mathrm{xc}}[\rho]$$

$$v_s[\rho](\mathbf{r}) = v(\mathbf{r}) + v_{\mathrm{H}}[\rho](\mathbf{r}) + v_{\mathrm{xc}}[\rho](\mathbf{r}) + \Delta\mu$$

$$v_{\mathrm{H}}(\mathbf{r}) := \int \mathrm{d}\mathbf{r}'\, \rho(\mathbf{r}')w(|\mathbf{r} - \mathbf{r}'|) \qquad v_{\mathrm{xc}}(\mathbf{r}) := \frac{\delta E_{\mathrm{xc}}}{\delta \rho(\mathbf{r})}$$

How to model $W_{\mathrm{xc}}[\rho]$?

$$W = \frac{1}{2}\int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 \, \frac{P(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

- W: interaction of N particles with N-1 particles
- W_{H}: interaction of N particles with N particles

→ W_{xc}: interaction of N particles with -1 particle

Removal of self-interaction

The xc-hole

$$W_{\rm xc} = \frac{1}{2}\int d\mathbf{r}_1 \int d\mathbf{r}_2 \, \frac{P(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$= \frac{1}{2}\int d\mathbf{r}_{\rm ref} \int d\mathbf{r} \, \rho(\mathbf{r}_{\rm ref}) \frac{\rho_{\rm xc}(\mathbf{r}|\mathbf{r}_{\rm ref})}{|\mathbf{r}_{\rm ref} - \mathbf{r}|}$$

xc-hole: $\rho_{\rm xc}(\mathbf{r}|\mathbf{r}_{\rm ref}) = \frac{P(\mathbf{r}, \mathbf{r}_{\rm ref})}{\rho(\mathbf{r}_{\rm ref})} - \rho(\mathbf{r})$

$$\int d\mathbf{r} \, \rho_{\rm xc}(\mathbf{r}|\mathbf{r}_{\rm ref}) = -1$$

The x-hole

$$P_s(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) - \frac{1}{2}|\gamma_s(\mathbf{r}_1, \mathbf{r}_2)|^2$$

$$\rho_{\mathrm{x}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}}) = -\frac{1}{2}\frac{|\gamma_s(\mathbf{r}, \mathbf{r}_{\mathrm{ref}})|^2}{\rho(\mathbf{r}_{\mathrm{ref}})}$$

$$\int \mathrm{d}\mathbf{r}\ \rho_{\mathrm{x}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}}) = -1$$

$$\rho_{\mathrm{xc}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}}) = \rho_{\mathrm{x}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}}) + \rho_{\mathrm{c}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}})$$

$$\int \mathrm{d}\mathbf{r}\ \rho_{\mathrm{c}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}}) = 0$$

Example: H_2

$$1\sigma_g(\mathbf{r}) = \frac{1}{\sqrt{2(1+S)}}\big(1s_a(\mathbf{r}) + 1s_b(\mathbf{r})\big)$$

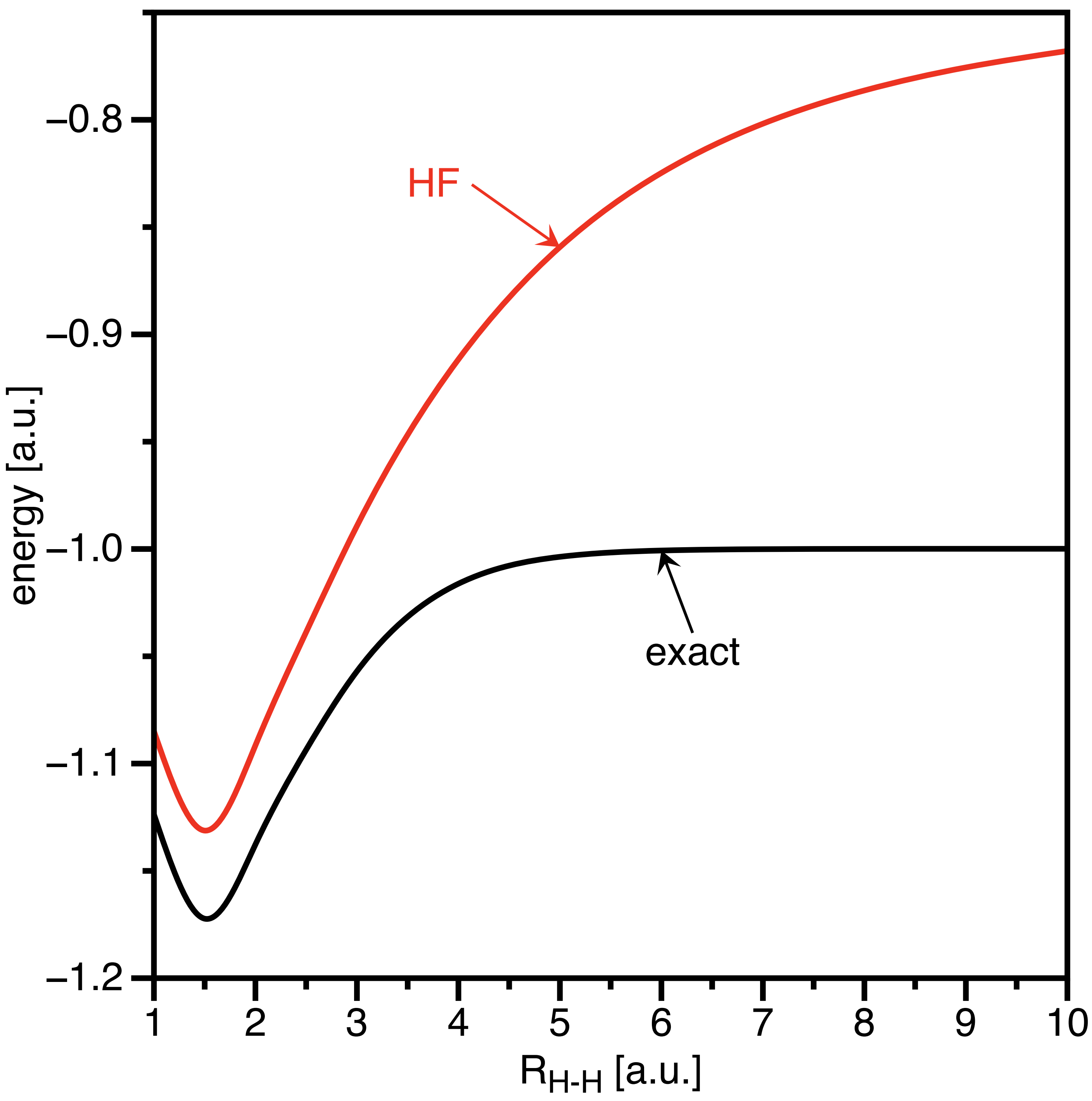
$$S \coloneqq \langle 1s_a | 1s_b \rangle$$

$$1\sigma_u(\mathbf{r}) = \frac{1}{\sqrt{2(1-S)}}\big(1s_a(\mathbf{r}) - 1s_b(\mathbf{r})\big)$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = c_g 1\sigma_g(\mathbf{r}_1) 1\sigma_g(\mathbf{r}_2) + c_u 1\sigma_u(\mathbf{r}_1) 1\sigma_u(\mathbf{r}_2) + \cdots$$

Hartree–Fock

Example: H_2



H_2 Kohn–Sham

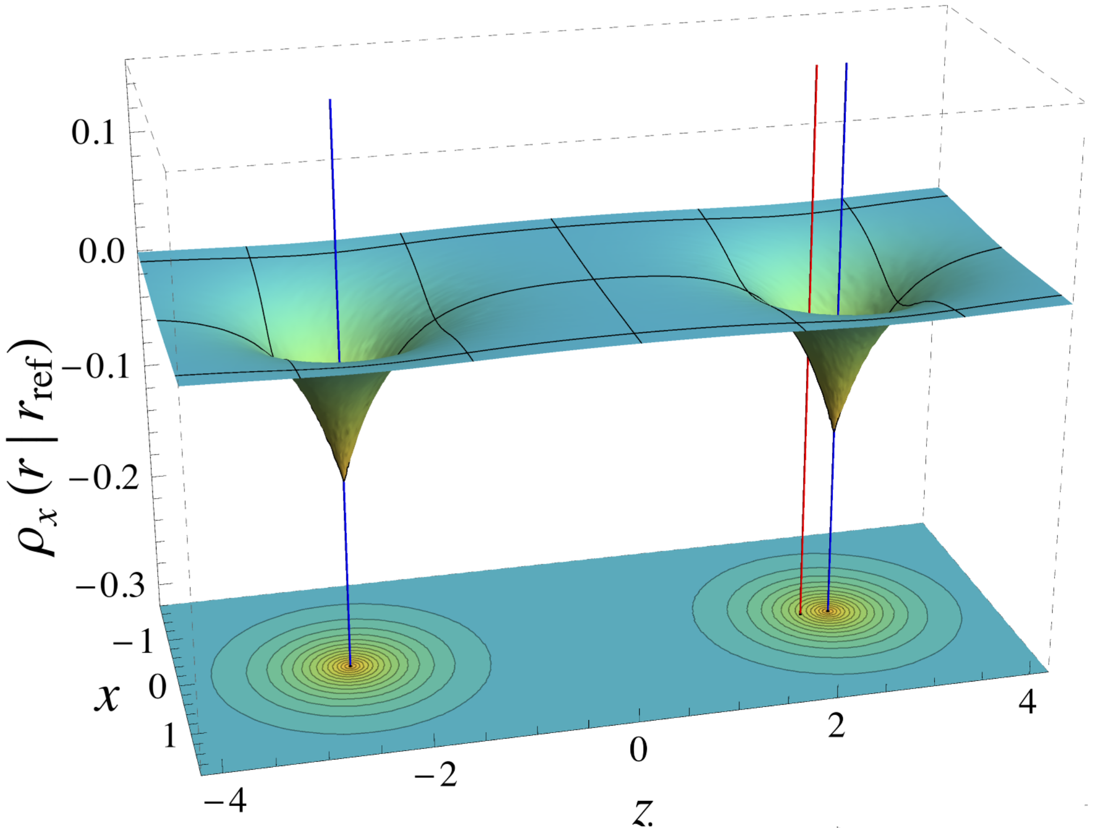
$$\rho(\mathbf{r}) = 2|\sigma_g(\mathbf{r})|^2 \quad \Rightarrow \quad \sigma_g(\mathbf{r}) = \sqrt{\rho(\mathbf{r})/2}$$

$$\gamma_s(\mathbf{r}, \mathbf{r}') = 2\sigma_g(\mathbf{r})\sigma_g(\mathbf{r}') = \sqrt{\rho(\mathbf{r})\rho(\mathbf{r}')}$$

$$\rho_{\mathrm{x}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}}) = -\frac{1}{2}\frac{|\gamma_s(\mathbf{r}, \mathbf{r}_{\mathrm{ref}})|^2}{\rho(\mathbf{r}_{\mathrm{ref}})} = -|\sigma_g(\mathbf{r})|^2 = -\frac{1}{2}\rho(\mathbf{r})$$

x-hole independent of r_{ref}!

H_2 holes at R_{H-H} = 5 Bohr



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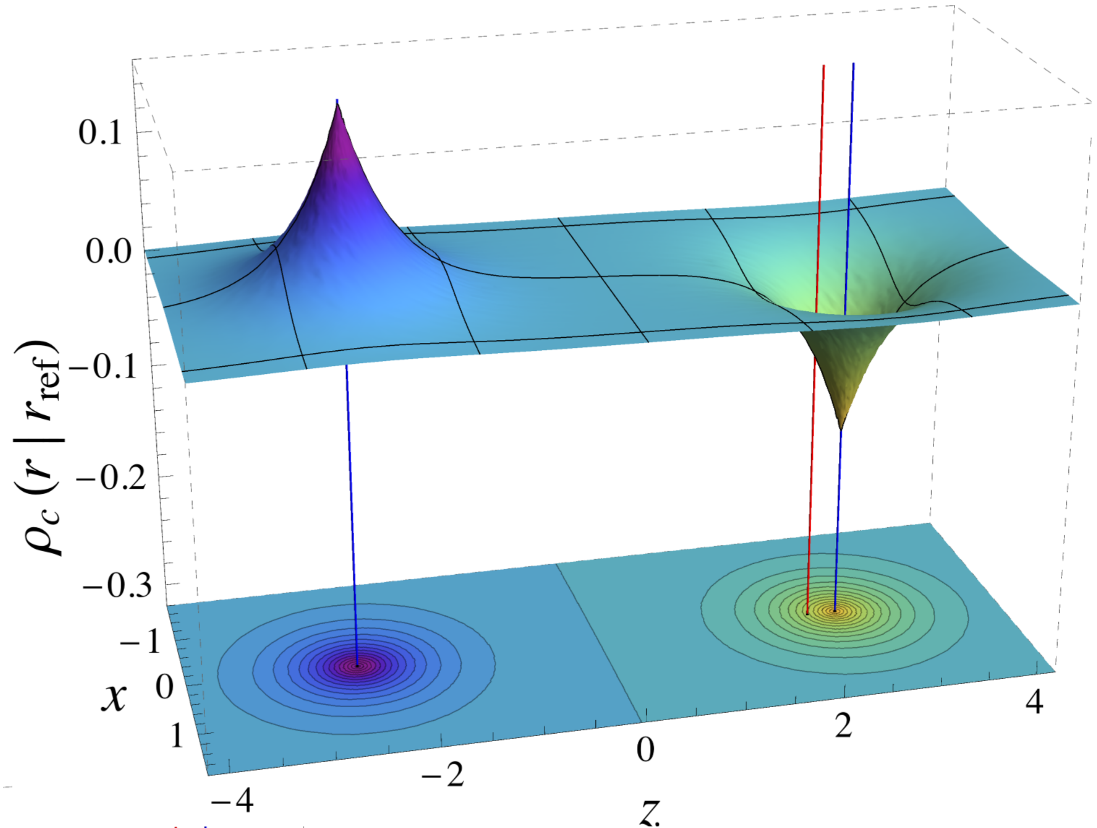

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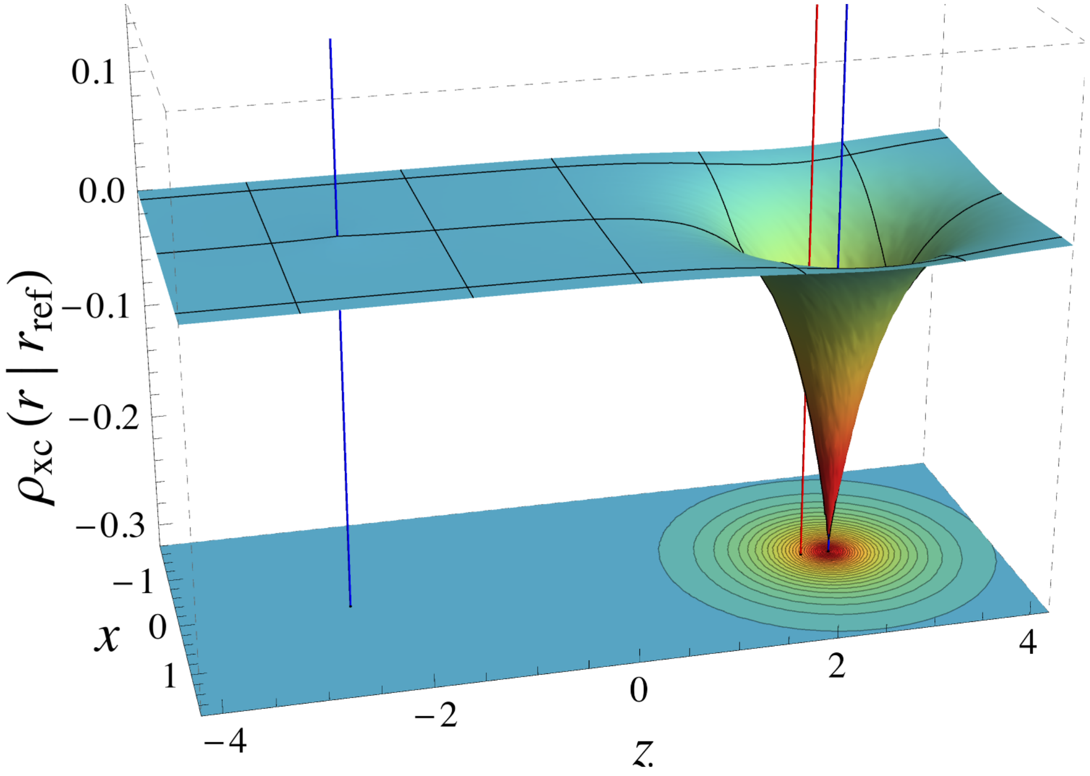
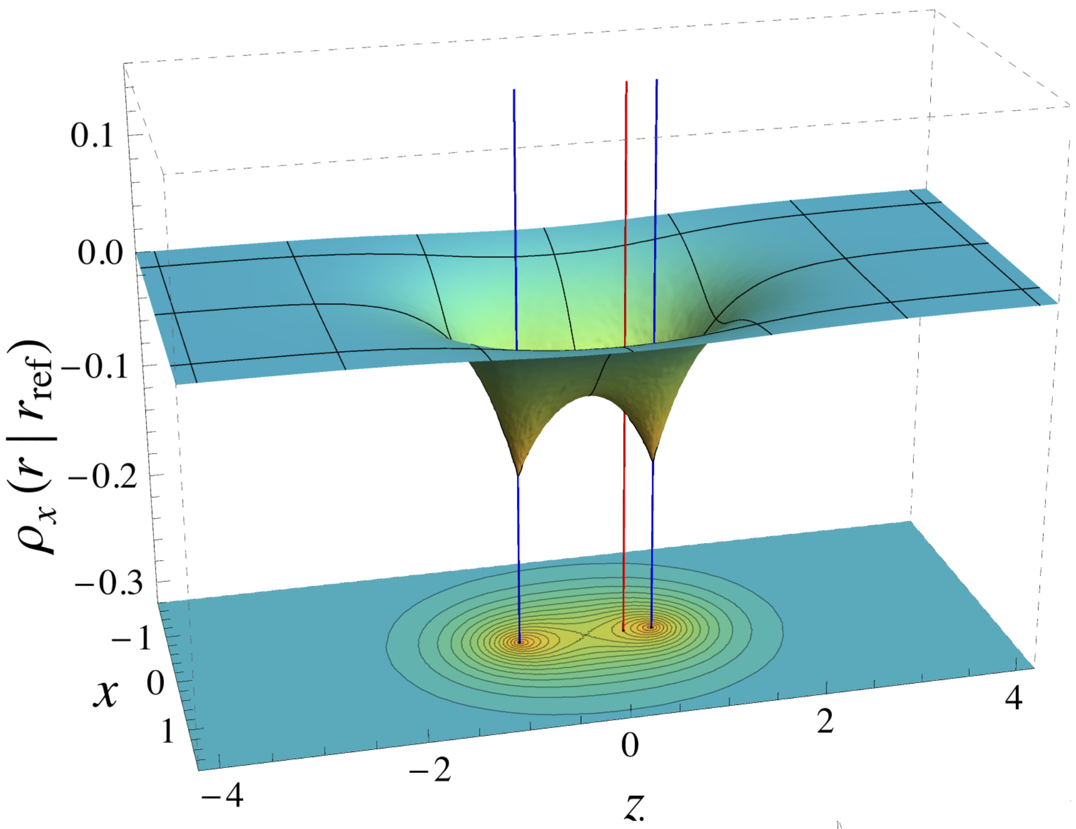


H_2 equilibrium holes



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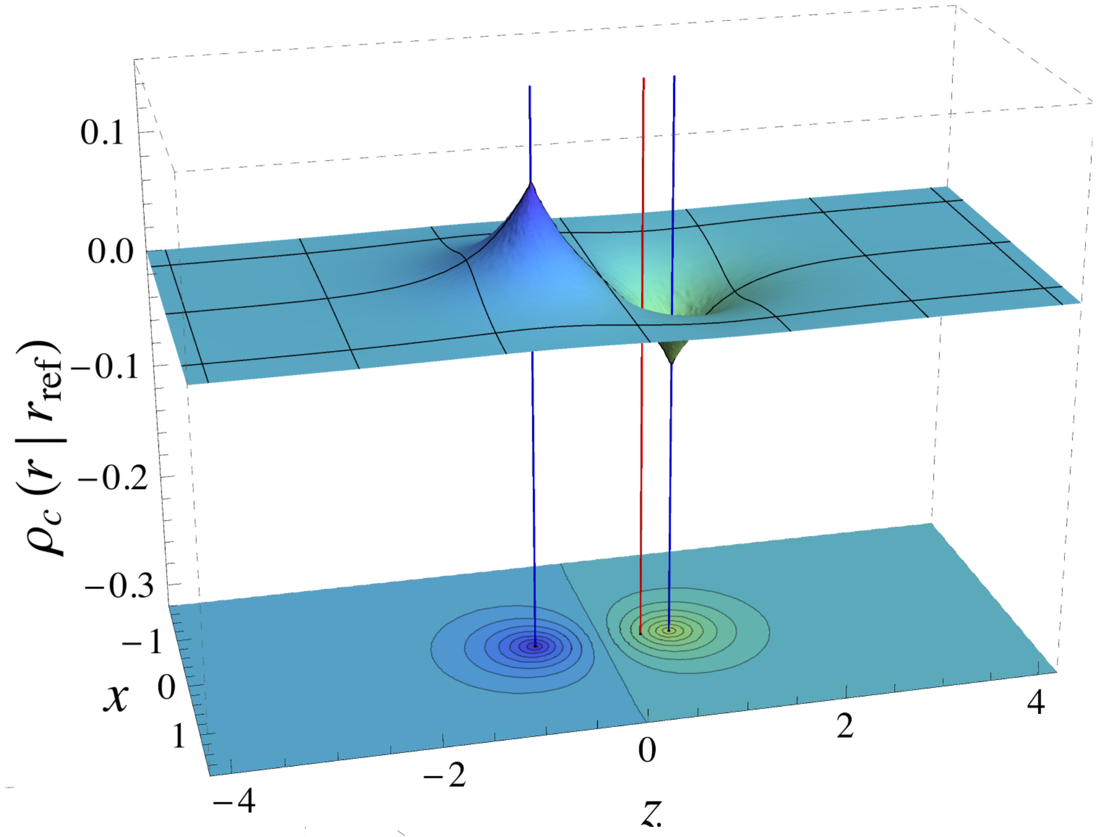

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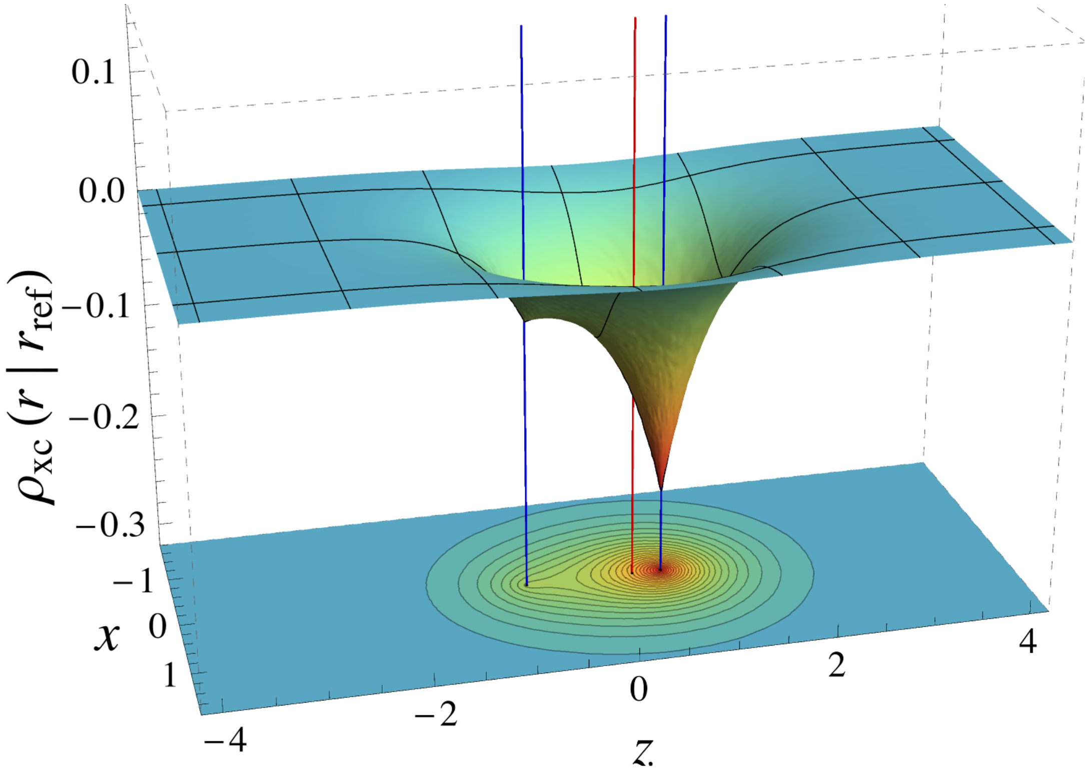


How to deal with $T_\mathrm{c}[\rho]$?

$\hat{H}_\lambda = \hat{T} + \hat{V}_\lambda + \lambda \hat{W}$ v_λ such that $\rho_\lambda = \rho_1$

$$\begin{aligned}\frac{\partial E_\lambda}{\partial \lambda} &= \left\langle \Psi_\lambda \middle| \frac{\partial \hat{H}_\lambda}{\partial \lambda} \middle| \Psi_\lambda \right\rangle \\ &= \left\langle \Psi_\lambda \middle| \frac{\partial \hat{V}_\lambda}{\partial \lambda} \middle| \Psi_\lambda \right\rangle + \left\langle \Psi_\lambda \middle| \hat{W} \middle| \Psi_\lambda \right\rangle \\ &= \int \mathrm{d}\mathbf{r} \, \frac{\partial v_\lambda(\mathbf{r})}{\partial \lambda} \rho(\mathbf{r}) + \\ &\quad \frac{1}{2} \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 \, P_\lambda(\mathbf{r}_1, \mathbf{r}_2) w(\mathbf{r}_1, \mathbf{r}_2)\end{aligned}$$

C.O. Almbladh, Tech. Rep. (University of Lund, 1972)
D.C. Langreth and J.P. Perdew, Solid State Commun. **17**, 1425 (1975)

Fundamental theorem of calculus

$$T + V + W - T_s - V_s$$

$$\boxed{E_1 - E_0} = \int_0^1 \mathrm{d}\lambda \, \frac{\partial E_\lambda}{\partial \lambda}$$

$$V - V_s$$

$$= \boxed{\int \mathrm{d}\mathbf{r} \, \big(v_1(\mathbf{r}) - v_0(\mathbf{r})\big)\rho(\mathbf{r})} + \frac{1}{2}\int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 \, \bar{P}(\mathbf{r}_1, \mathbf{r}_2) w(\mathbf{r}_1, \mathbf{r}_2)$$

$$\bar{P}(\mathbf{r}_1, \mathbf{r}_2) := \int_0^1 \mathrm{d}\lambda \, P_\lambda(\mathbf{r}_1, \mathbf{r}_2)$$

$$\boxed{E_{\mathrm{xc}} = \frac{1}{2}\int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 \, \big(\bar{P}(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\big) w(\mathbf{r}_1, \mathbf{r}_2)}$$

Averaged xc-hole

exchange-correlation energy:

$$\begin{aligned} E_{\mathrm{xc}} &= \frac{1}{2}\int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 \, \big(\bar{P}(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\big) w(|\mathbf{r}_1 - \mathbf{r}_2|) \\ &= \frac{1}{2}\int \mathrm{d}\mathbf{r}_{\mathrm{ref}} \int \mathrm{d}\mathbf{r} \, \rho(\mathbf{r}_{\mathrm{ref}}) \frac{\bar{\rho}_{\mathrm{xc}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}})}{|\mathbf{r}_{\mathrm{ref}} - \mathbf{r}|} \end{aligned}$$

averaged xc-hole: $\bar{\rho}_{\mathrm{xc}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}}) \coloneqq \dfrac{\bar{P}(\mathbf{r}, \mathbf{r}_{\mathrm{ref}})}{\rho(\mathbf{r}_{\mathrm{ref}})} - \rho(\mathbf{r})$

Local Density Approximation (Perdew: LSD)

$$E_{\mathrm{xc}} = \frac{1}{2}\int \mathrm{d}\mathbf{r}_{\mathrm{ref}} \int \mathrm{d}\mathbf{r}\; \rho(\mathbf{r}_{\mathrm{ref}}) \frac{\bar{\rho}_{\mathrm{xc}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}})}{|\mathbf{r}_{\mathrm{ref}} - \mathbf{r}|}$$

The Coulomb interaction mainly probes the region close to the reference positions.

If density does not vary too much, we can approximate the density to have the constant value of the one at the reference position

Homogeneous Electron Gas

$$\bar{\rho}_{\mathrm{xc}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}}) \approx \bar{\rho}_{\mathrm{xc}}^{\mathrm{LDA}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}}) = \bar{\rho}_{\mathrm{xc}}^{\mathrm{HEG}}\big(\rho(\mathbf{r}_{\mathrm{ref}}), |\mathbf{r} - \mathbf{r}_{\mathrm{ref}}|\big)$$

Local Density Approximation

$$\gamma_s(r_{12}, k_F) = \frac{k_F^3}{\pi^2}\frac{\sin(k_F r_{12}) - k_F r_{12}\cos(k_F r_{12})}{(k_F r_{12})^3}$$

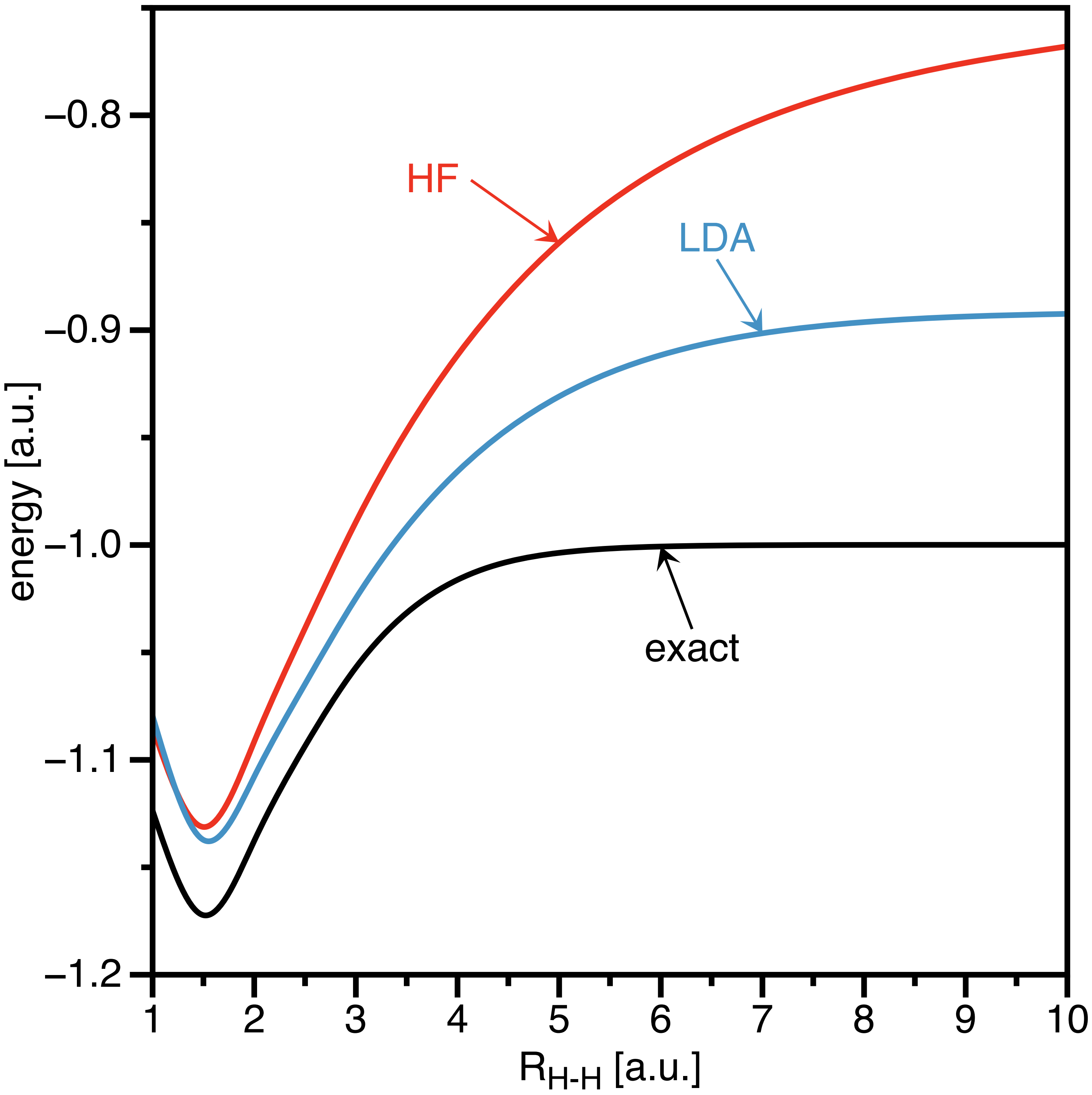
$$k_F := \sqrt[3]{3\pi^2\rho}$$

$$\rho_{\mathrm{x}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}}) = -\frac{1}{2}\frac{\left|\gamma_s(\mathbf{r}, \mathbf{r}_{\mathrm{ref}})\right|^2}{\rho(\mathbf{r}_{\mathrm{ref}})}$$

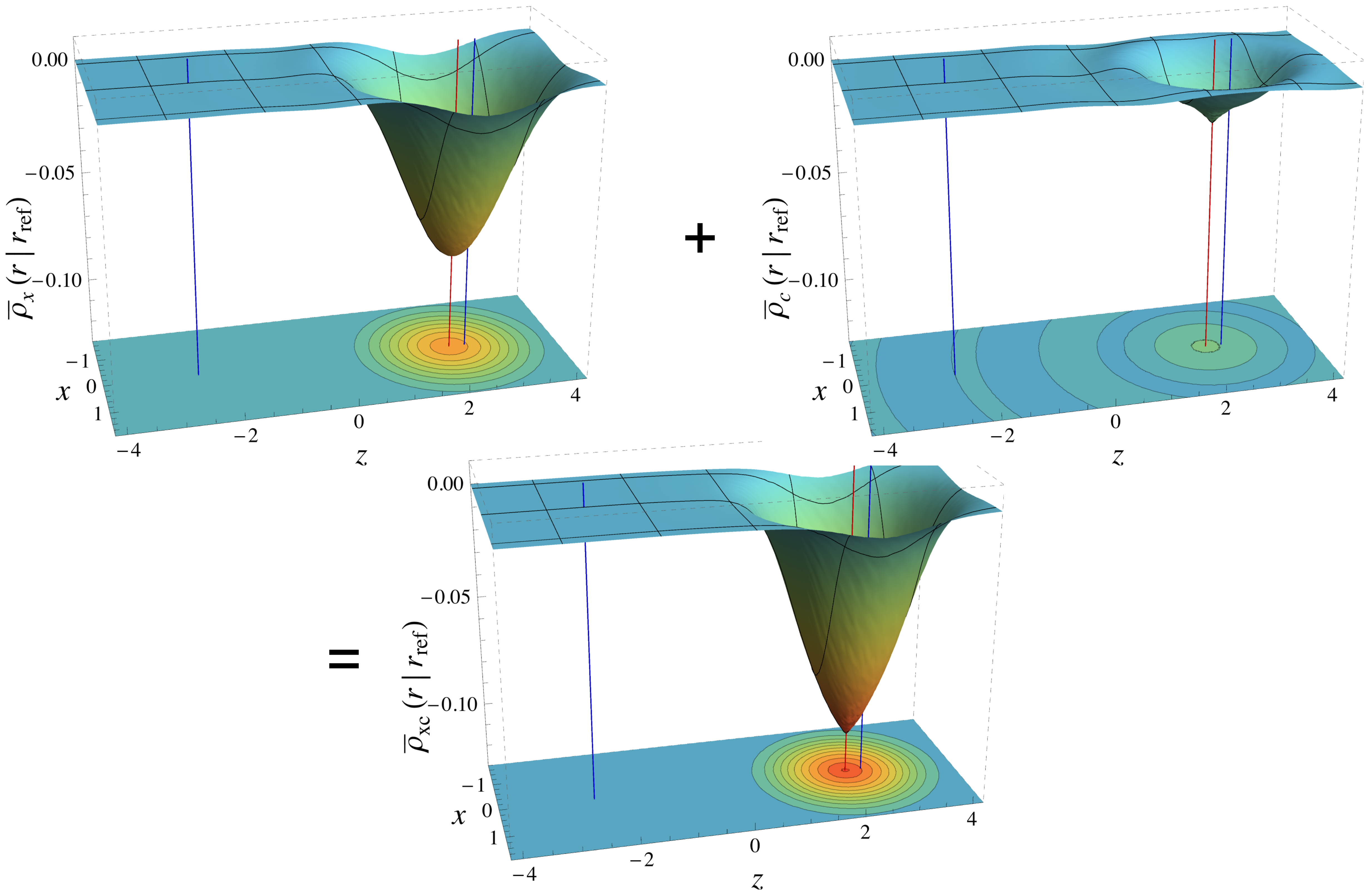
$$E_x = -\alpha\sqrt[3]{\frac{3}{8\pi}}\int \mathrm{d}\mathbf{r}\;\rho(\mathbf{r})^{\frac{4}{3}} \qquad\qquad \alpha = \frac{2}{3}$$

$\bar{\rho}_{\mathrm{c}}^{\mathrm{HEG}}$ from parametrised QMC data

LDA energy for H_2



H_2 LDA holes at $R_{H–H}$ = 5 Bohr



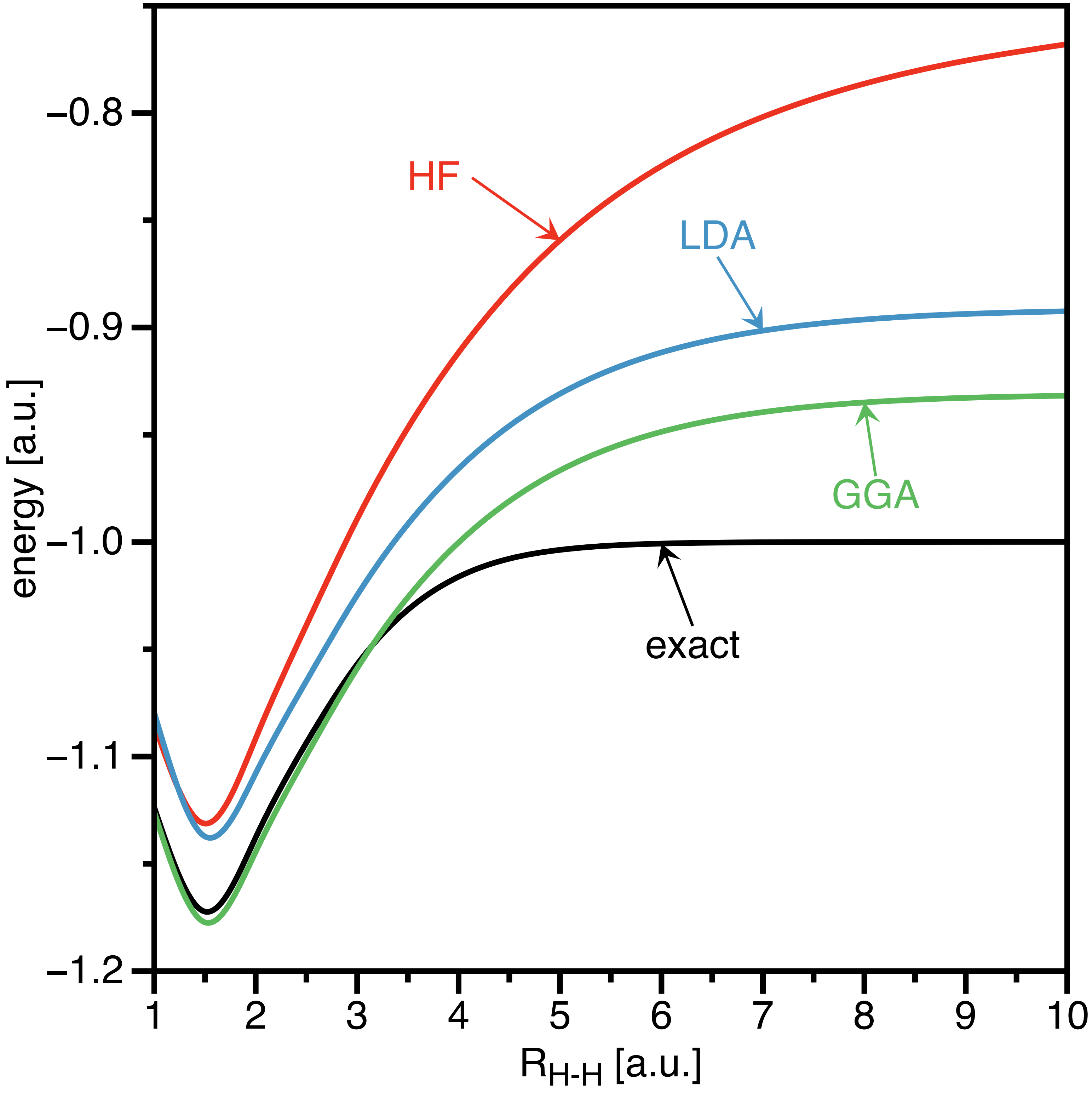
LDA summary

- Bad approximation to x-hole and c-hole
- Decent approximation to full xc-hole
- Slater’s Xα method α=2/3 → 0.7 (1963)
- Usually better than HF and cheaper!

Include gradients (GGA)

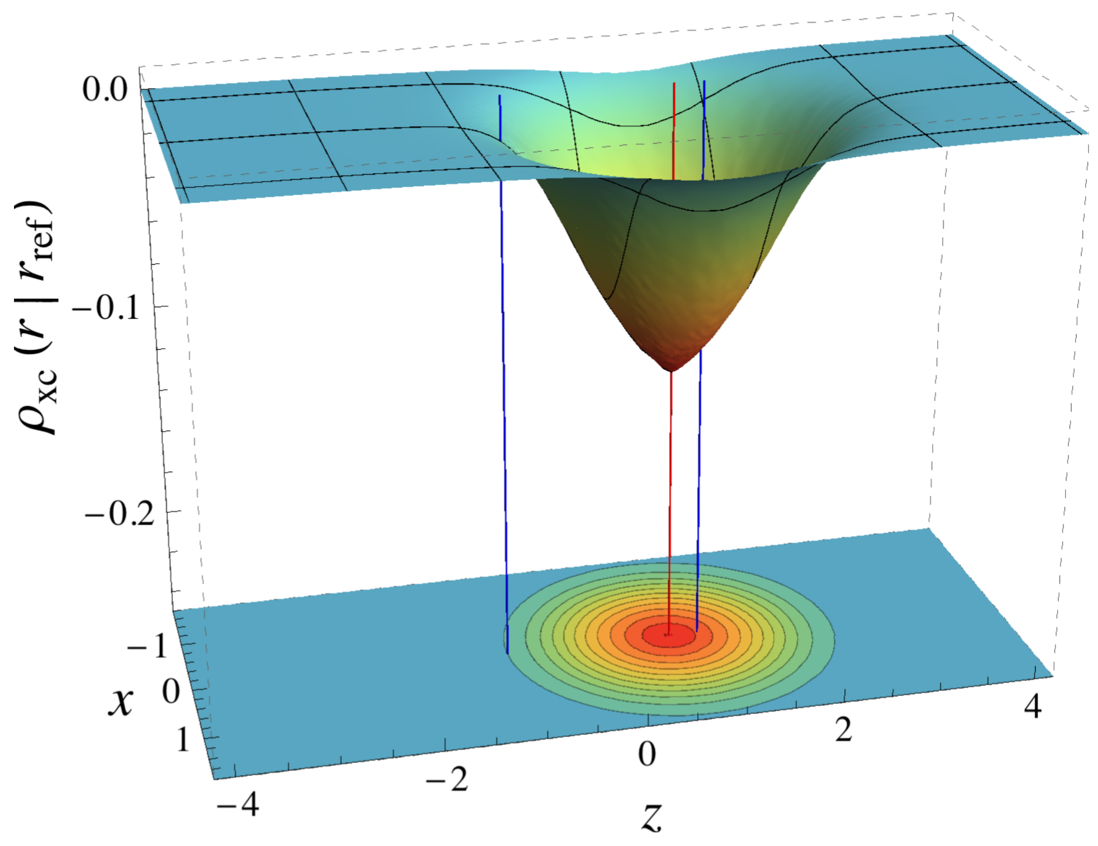
- Gradient Expansion Approximation
- GEA’s fail due to oscillations (Perdew)
- Generalized Gradient Approximation:
  - cut-off oscillations
  - renormalize hole to -1
- Becke’s fit to atoms made DFT popular in chemistry

GGA energy for H_2

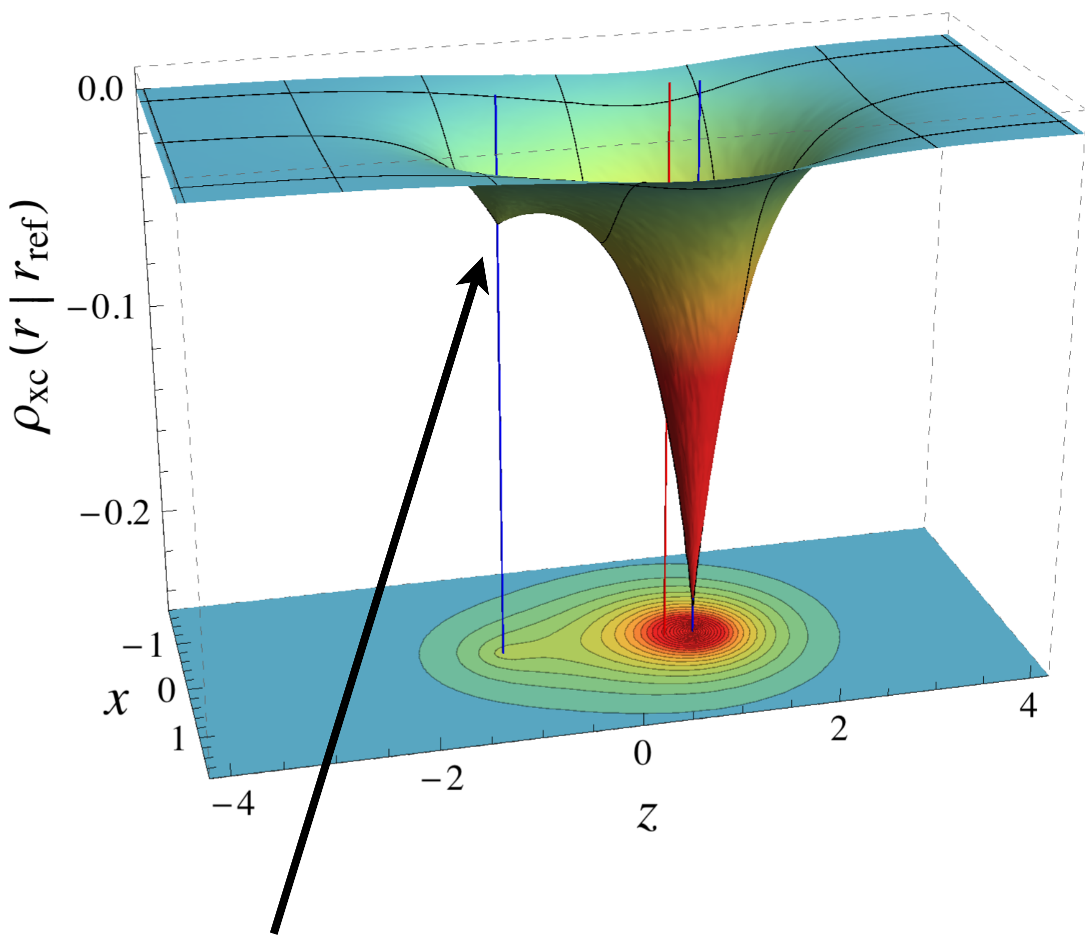


Include “exact” exchange?

LDA-hole



exact hole



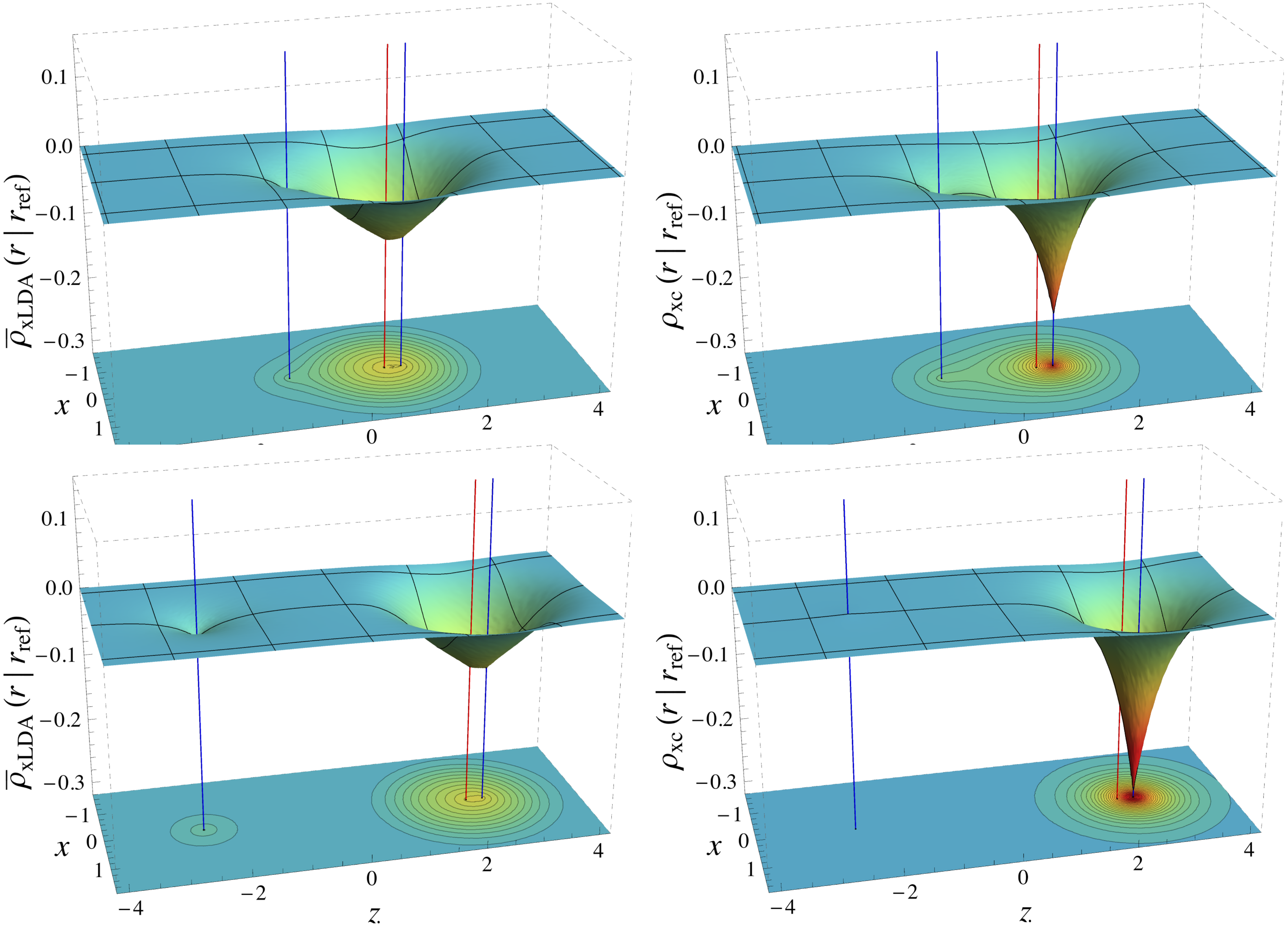
Only fractional amount needed ≈ 20%

$$\rho_{\mathrm{x}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}}) = -\frac{1}{2}\frac{|\gamma_s(\mathbf{r},\mathbf{r}_{\mathrm{ref}})|^2}{\rho(\mathbf{r}_{\mathrm{ref}})}$$

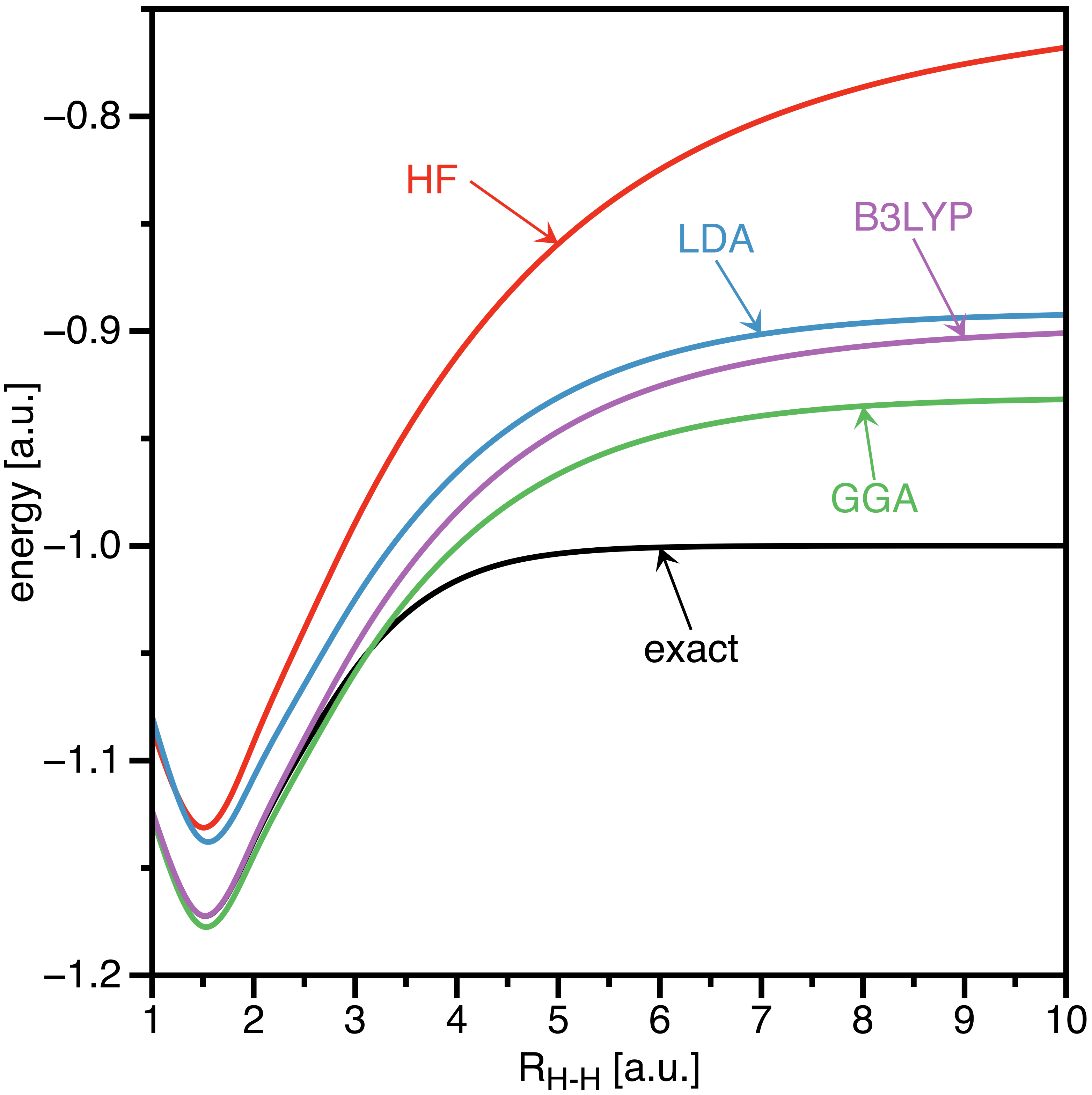
H_2 xLDA (20%) holes

$R_{H–H}$ =
2 Bohr

$R_{H–H}$ =
5 Bohr



H_2 B3LYP (20% E_x) energy



Approximations in 1RDM functional theory

- Kinetic energy is exact, no KS system needed
- No difficult stuff with a coupling constant integration needed to include kinetic correlation effects
- We can just work with the plain xc-hole: $\rho_{\mathrm{xc}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}})$.

Exact 1RDM functionals

Pure state functional (Levy)

$$W_{\mathrm{L}}[\gamma] = \min_{\Psi \to \gamma} \langle \Psi | \hat{W} | \Psi \rangle$$

Mixed state functional (Valone)

$$W_{\mathrm{V}}[\gamma] = \min_{\hat{\rho} \to \gamma} \mathrm{Tr}\big\{\hat{\rho}\hat{W}\big\}$$

$$\mathrm{Tr}\{\cdot\} = \sum_K \langle \Psi_K | \cdot | \Psi_K \rangle \qquad \hat{\rho} = \sum_K w_K |\Psi_K\rangle\langle\Psi_K|$$

weights: $\sum_K w_K = 1$ $\qquad 0 \leq w_K (\leq 1)$

Two-electrons (singlet)

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \Psi(\mathbf{r}_1, \mathbf{r}_2)\Sigma(\sigma_1, \sigma_2)$$

singlet: symmetric anti-symmetric

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_k c_k \phi_k(\mathbf{r}_1)\phi_k(\mathbf{r}_2)$$

- eigenfunctions are NOs
- eigenvalues related to occupations as $|c_k|^2 = n_k$

P.-O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956)

Exact singlet functional (Löwdin–Shull)

$$W_{\mathrm{L}}[\gamma] = \min_{\{\alpha_i\}} \sum_{kl} \mathrm{e}^{\mathrm{i}(\alpha_k - \alpha_l)} \sqrt{n_k n_l}\ \langle \phi_k \phi_k | \phi_l \phi_l \rangle$$

$$\langle \phi_k \phi_l | \phi_m \phi_n \rangle := \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2\ \frac{\phi_k^*(\mathbf{r}_1)\phi_l^*(\mathbf{r}_2)\phi_m(\mathbf{r}_1)\phi_n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

- Good approximation $f_1 = +1$ and $f_{i>1} = -1$
- However, for Van der Waals need alternating signs

P.-O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956)
KG and R. Van Leeuwen, J. Chem. Phys. **139**, 104110 (2013)

Hartree-Fock

$$W^{\mathrm{HF}}[\gamma] = \frac{1}{2}\sum_{rs} n_r n_s \langle \phi_r \phi_s | \phi_r \phi_s \rangle - \frac{1}{2}\sum_{rs} n_r n_s \langle \phi_r \phi_s | \phi_s \phi_r \rangle$$

Coulomb

Exchange

Integral of HF x-hole

$$\int \mathrm{d}\mathbf{r}\, \rho_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r}|\mathbf{r}_{\mathrm{ref}}) = -\frac{1}{\rho(\mathbf{r}_{\mathrm{ref}})} \sum_r n_r^2 |\phi_r(\mathbf{r}_{\mathrm{ref}})|^2$$

- Only integrates to -1 for idempotent 1RDM ($n_r^2 = n_r$).
- Change the power to make it always correct

Müller = Buijse Baerends functional

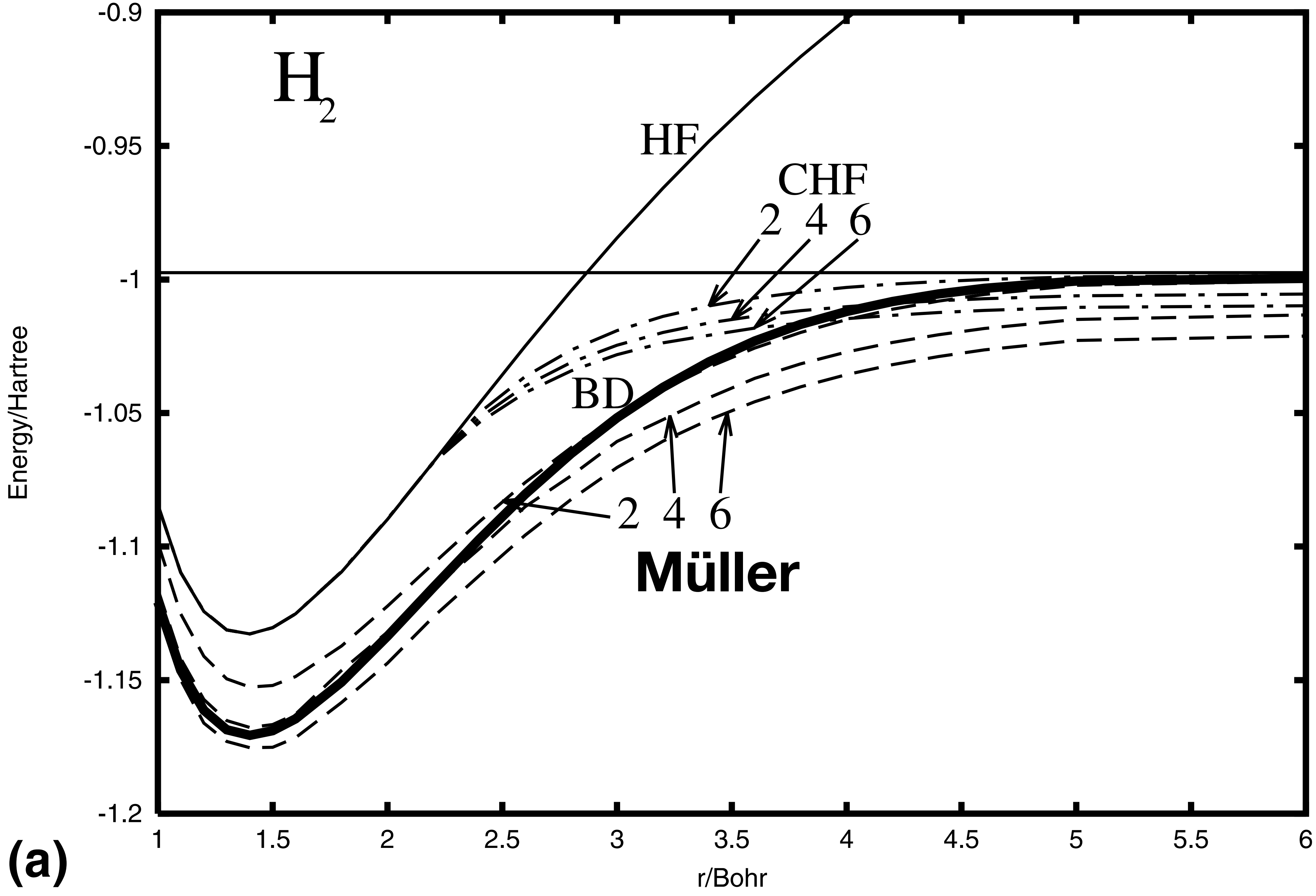
$$W^{\mathrm{M}}[\gamma] = \frac{1}{2}\sum_{rs} n_r n_s \langle \phi_r \phi_s | \phi_r \phi_s \rangle - \frac{1}{2}\sum_{rs} \sqrt{n_r n_s} \langle \phi_r \phi_s | \phi_s \phi_r \rangle$$

$P(\mathbf{x}_1, \mathbf{x}_2) \ngeq 0$ → no variational upper bound

For 2 electrons variational lower bound, i.e. $E^{\mathrm{M}} \leq E^{\mathrm{exact}}$

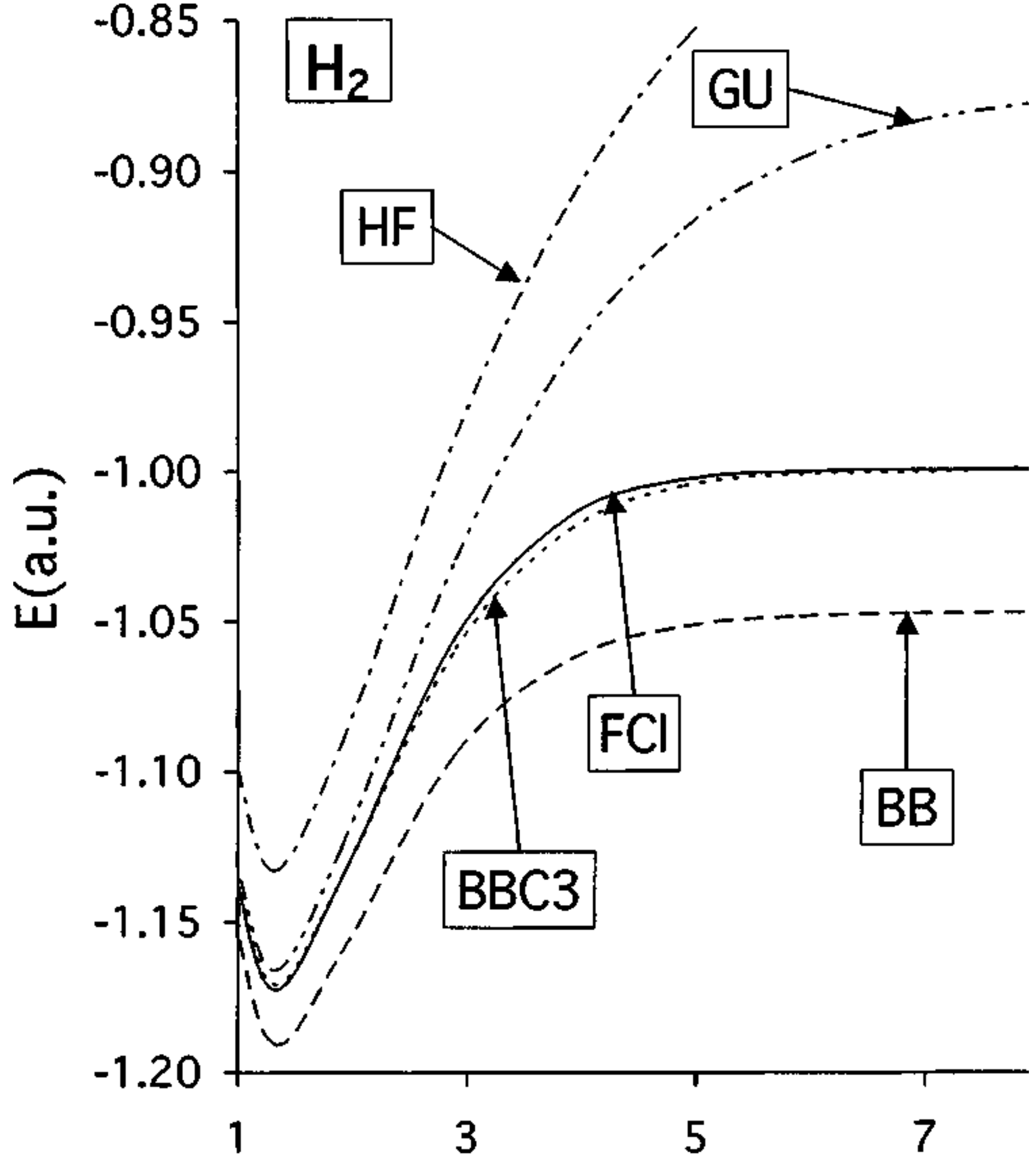
Conjecture: Always a lower bound for energy

M=BB for H_2



A. Cohen and E.J. Baerends, Chem. Phys. Lett. **364**, 409 (2002)

BBCorrected (repulsive modifications)



O. Gritsenko, K. Pernal and E.J. Baerends, J. Chem. Phys. **122**, 204102 (2005)

Anti-symmerised strongly orthogonal geminals (APSG)

$$\Psi^{\mathrm{APSG}}(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \hat{A} \prod_{r=1}^{N/2} \psi_r^{\mathrm{LS}}(\mathbf{x}_1, \mathbf{x}_2)$$

anti-symmetriser

Geminal = 2-electron function

Strongly orthogonal geminals:

$$\int \mathrm{d}\mathbf{x}_2 \, \psi_r^{\mathrm{LS}*}(\mathbf{x}_1, \mathbf{x}_2) \psi_s^{\mathrm{LS}}(\mathbf{x}_1', \mathbf{x}_2) = 0 \text{ if } r \neq s$$

Anti-symmerised strongly orthogonal geminals (APSG)

Strongly orthogonality of the geminals implies:

$$\psi_r^{\mathrm{LS}}(\mathbf{x}_1, \mathbf{x}_2) = \sum_{i \in I_r} c_i \phi_i(\mathbf{x}_1) \phi_i(\mathbf{x}_2)$$

NOs

Disjoint subsets

Each geminal has its own ‘private’ NO space

$|c_i|^2 = n_i$ Löwdin-Shull (two-electron) like expansion

Anti-symmerised strongly orthogonal geminals (APSG)

Intra-geminal term (LS like)

$$W^{\mathrm{APSG}} = \frac{1}{2}\sum_{p,q} \delta_{I_p,I_q} c_p c_q \langle pp|qq\rangle +$$

$$\frac{1}{2}\sum_{p,q}(1-\delta_{I_p,I_q})|c_p|^2|c_q|^2\left[\langle pq|pq\rangle - \langle pq|qp\rangle\right]$$

Inter-geminal term (HF-like)

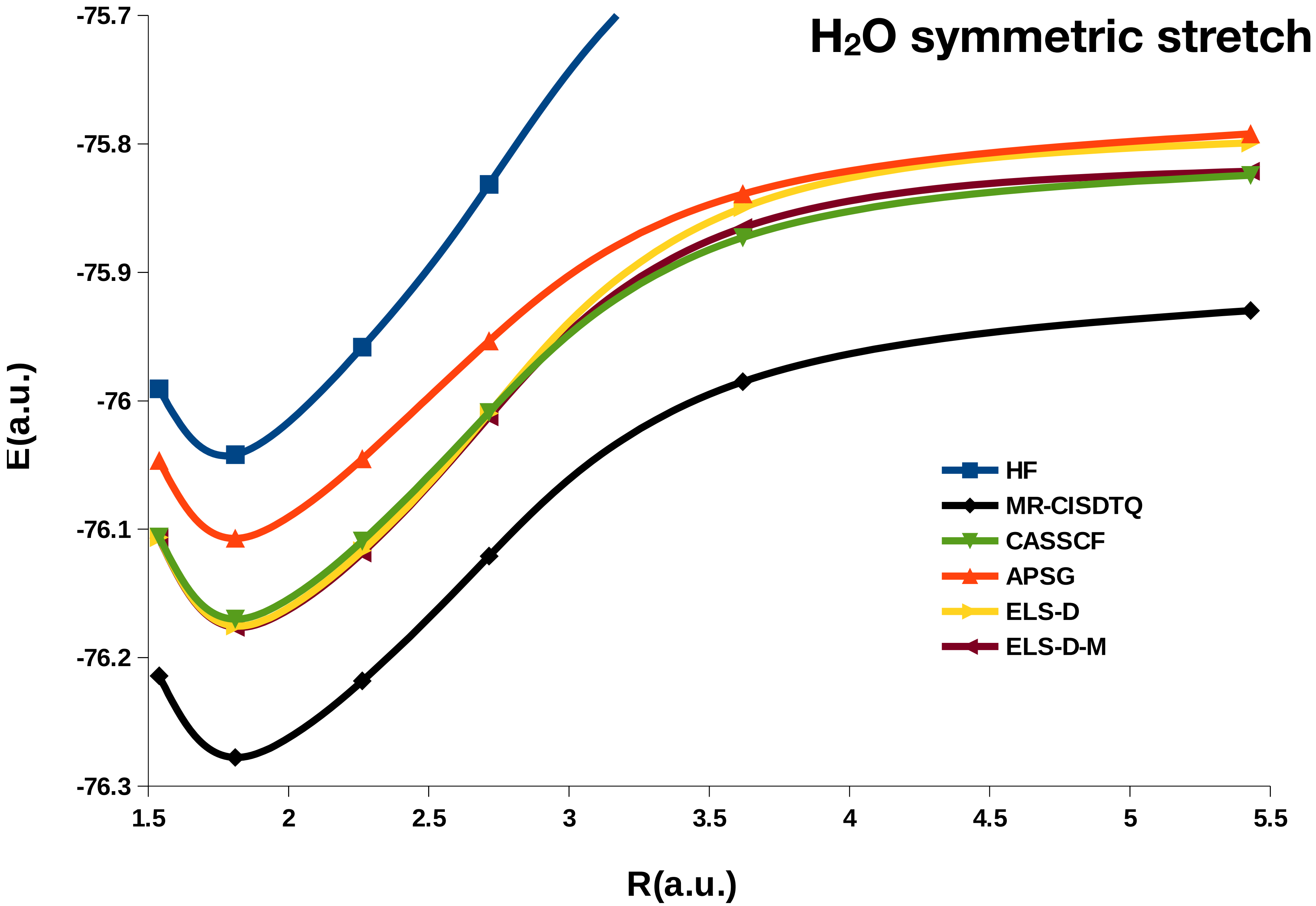
Within one geminal

$$c_p = +\sqrt{n_p} \text{ and } c_{q\neq p} = -\sqrt{n_q}$$

Inter-geminal correlation

- Via perturbation theory (Piris)
- Via fluctuation dissipation theorem (Pernal)
- Via linearised coupled cluster (Surján, Ayers)
- Learn from accurate calculations which additional terms are required (Meer, Gritsenko, Baerends)

Inter-geminal correlation



R. Van Meer, O.V. Gritsenko and E.J. Baerends, J. Chem. Phys. **148**, 104102 (2018)

Summary

- Kohn-Sham system needed to give reasonable kinetic energy functional: crucial for success of DFT
- Rationalisation of xc-functional via xc-hole
- Kinetic energy effects included via coupling constant integration
- Kinetic energy functional is explicit in 1RDM-FT: no KS & coupling constant integration needed
- Approximate 1RDM functionals via xc-hole models or augmentation of specific wave-function models (APSG)