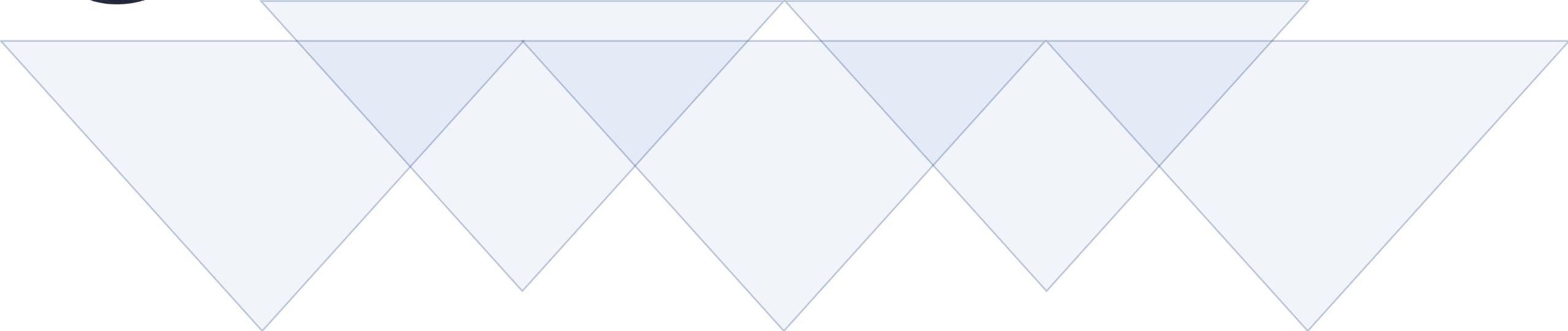


Density Functional Theory:

A short introduction



Contents of this lecture

Underlying theory:

- a. Hohenberg-Kohn theorem
- b. Orbital-free DFT
- c. Kohn-Sham DFT
- d. The exchange-correlation functional

Key questions to address:

- 1. What is DFT and why is it so popular?
- 2. How is a functional constructed?
- 3. What are the current problems with DFT to watch out for?

Introduction to DFT

$$F \left[\begin{array}{c} \text{H}_2\text{O molecule} \\ \text{electron density distribution} \end{array} \right] \stackrel{\text{same information}}{=} \hat{H}\Psi$$

Function: $f(x) = \text{number}$

Functional: $F[f] = \text{number}$

Hohenberg-Kohn theorem: $\rho(r)$ and Ψ are inherently linked

Solving the Hamiltonian exactly for an approximate WF $\propto N^4$

Solving an approximate Hamiltonian for an approximate $\rho \propto N^3$

So, if \hat{H} and ρ are known accurately, DFT is *faster* than WFT for the same accuracy

Orbital-free DFT: Thomas-Fermi-Dirac DFT

$$E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho]$$

$$\downarrow$$

$$= J[\rho] + K[\rho]$$

- Exchange energy correct
- KE underestimated by ~10%

note: no correlation term necessary!

$$J \quad -\cdots r \cdots - \quad P(r) \propto \frac{1}{r}$$

$J[\rho]$: **Coulomb** (classical repulsion of electrons)

$$K \quad \uparrow \cdots r \cdots \uparrow \quad P_{r=0} = 0$$

$K[\rho]$: **Exchange** (electrons with same quantum numbers cannot occupy same space)

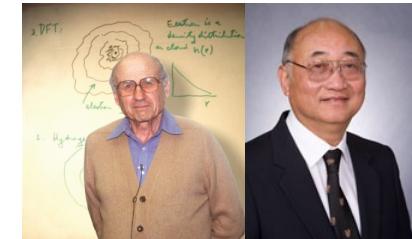
The Introduction of Orbitals: Kohn-Sham DFT

$$E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho]$$

exact small correction

$$T_{\text{exact}}[\rho] = \sum_i^N \left\langle \phi_i \left| -\frac{1}{2} \nabla^2 \right| \psi_i \right\rangle \quad J[\rho] + K[\rho] + C[\rho]$$

c.f. HF orbitals



J  $P(r) \propto \frac{1}{r}$ $J[\rho]$: **Coulomb** (classical repulsion of electrons)

K  $P_{r=0} = 0$ $K[\rho]$: **Exchange** (electrons with same quantum numbers cannot occupy same space)

C $\Psi(1,2,\dots,n) \neq \Psi(1) \Psi(2) \dots \Psi(n)$ $C[\rho]$: **Correlation** (1e⁻ orbital approximation)

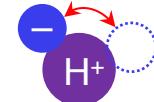
Fix KE problem, introduce smaller $C[\rho]$ problem (and increase the scaling)

Designing an Exchange Correlation Functional

$$E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] \quad \rightarrow \quad E[\rho] = T_{\text{exact}}[\rho] + V_{ne}[\rho] + J[\rho] + E_{xc}[\rho]$$

$$E_{xc} = E_x + E_c$$

- $K[\rho]$: e⁻s *less* likely to be found near to each other (h_x)
- $C[\rho]$: e⁻s *more* likely to be found further apart (h_c)

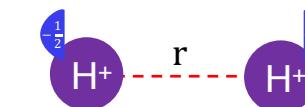


$$E_x + J[\rho] = 0$$

(Origin of self-interaction error)



not



$$E_x + E_c \rightarrow 0 \text{ as } r \rightarrow \infty$$

(Non-integer electron numbers)

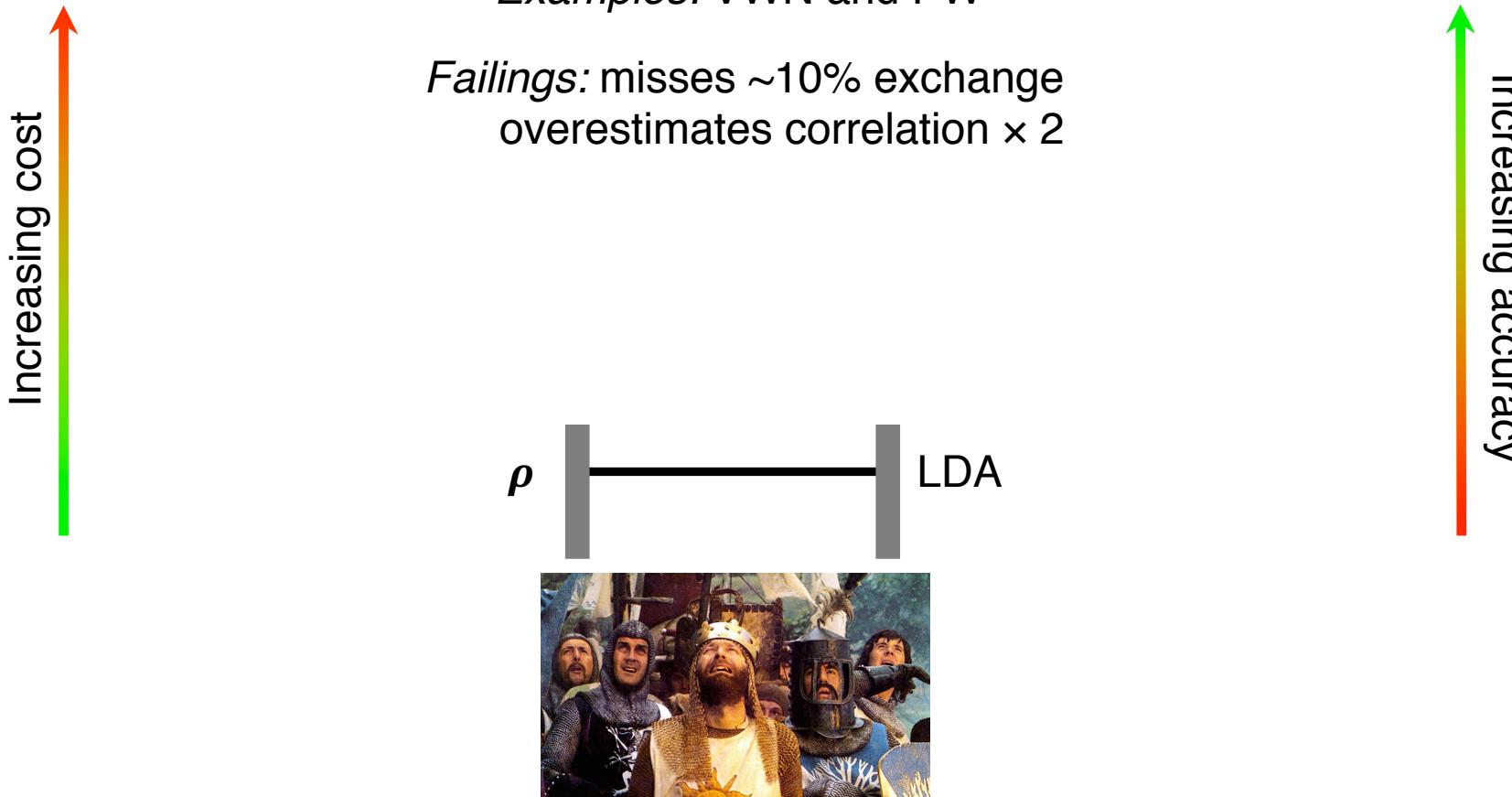
Jacob's Ladder of DFT: The First Rung (LDA)

Local (spin) density approximation: E_{xc} is a functional of ρ

Key approximation: Uniform electron gas

Examples: VWN and PW

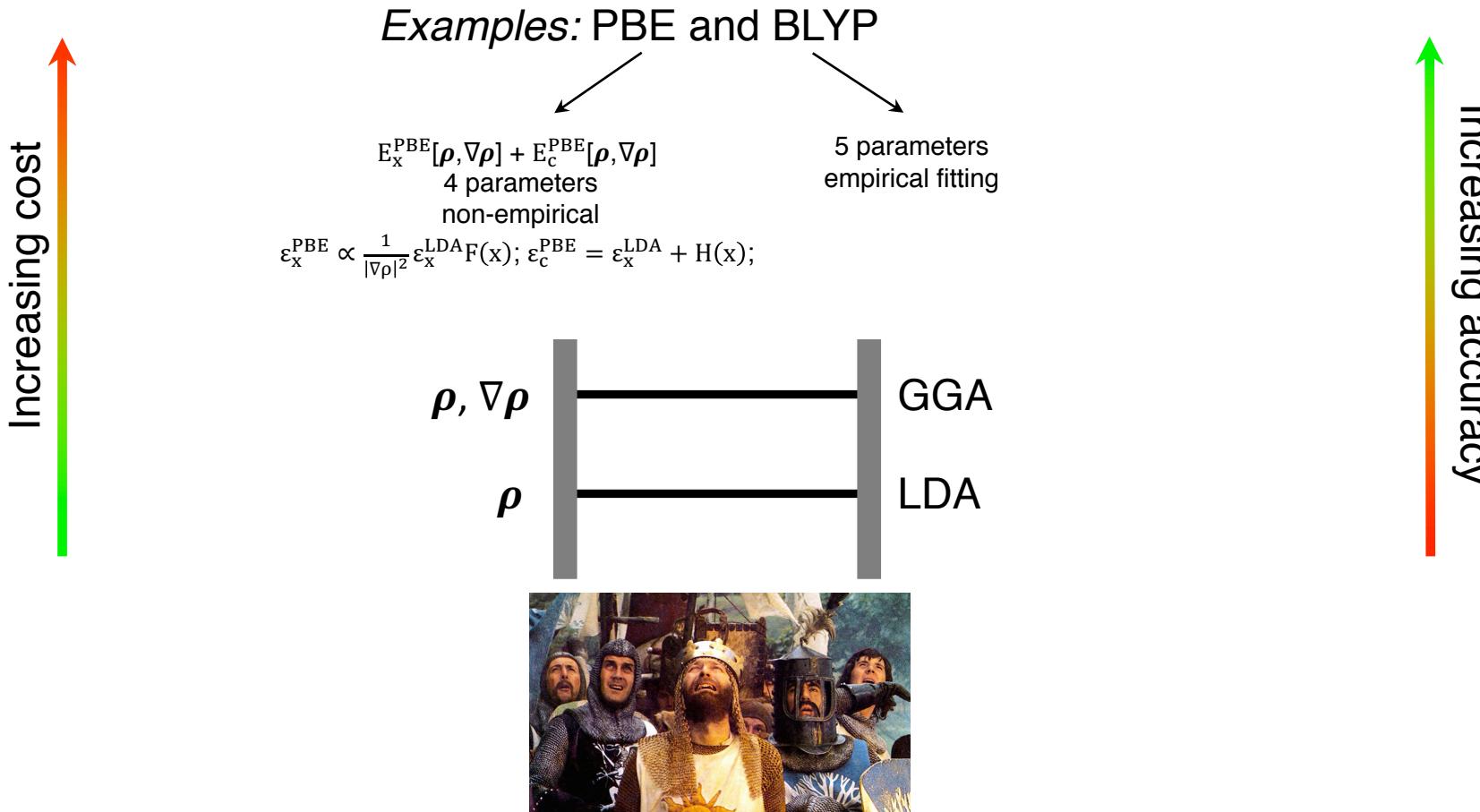
Failings: misses ~10% exchange
overestimates correlation $\times 2$



Jacob's Ladder of DFT: The Second Rung (GGA)

Generalised gradient approximation: E_{xc} is a functional of ρ and $\nabla\rho$

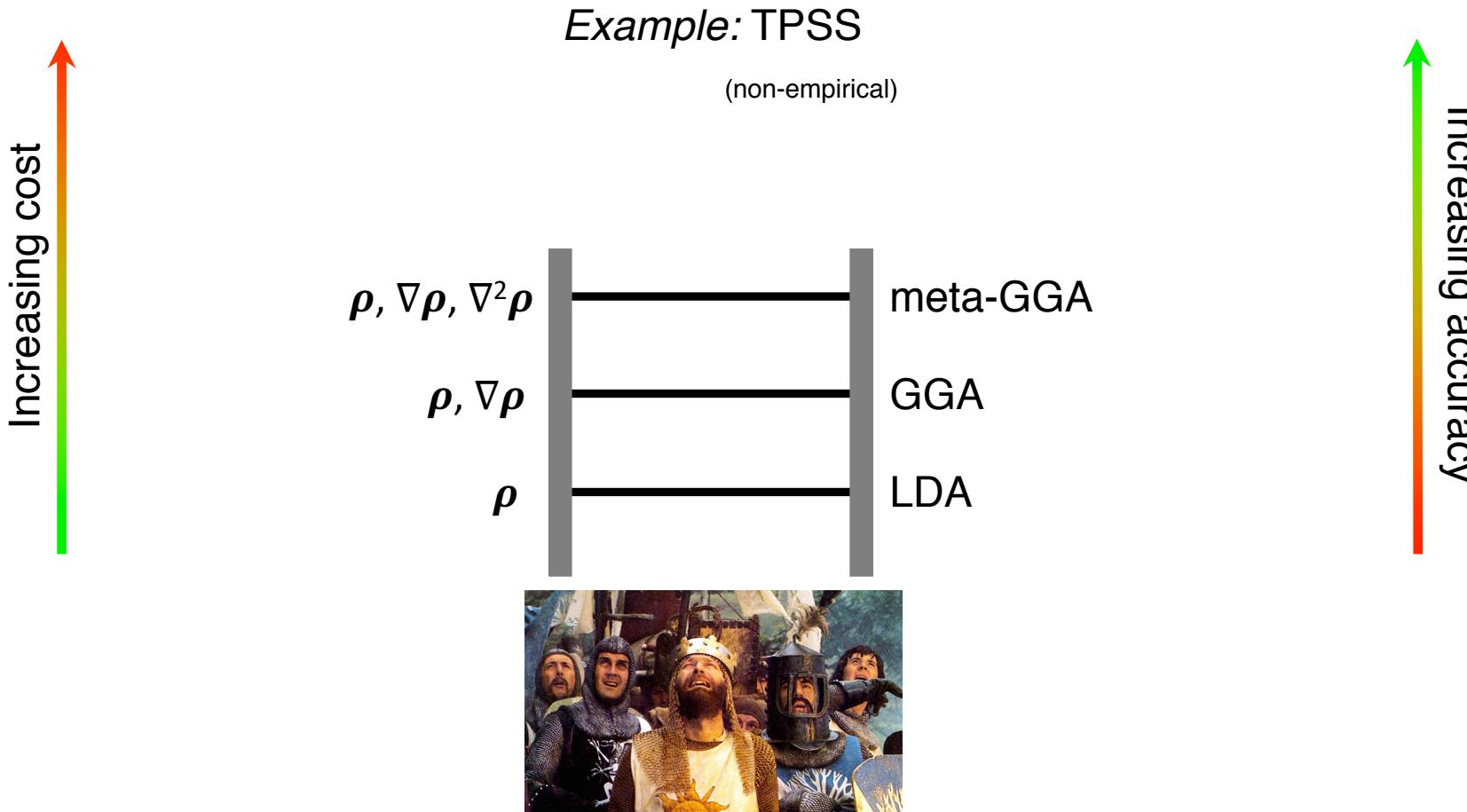
Key approximation: Non-uniform electron gas



Jacob's Ladder of DFT: The Third Rung (meta-GGA)

Meta-GGA: E_{xc} is a functional of ρ , $\nabla\rho$ and $\nabla^2\rho$

Key approximation: Inclusion of orbital kinetic energy



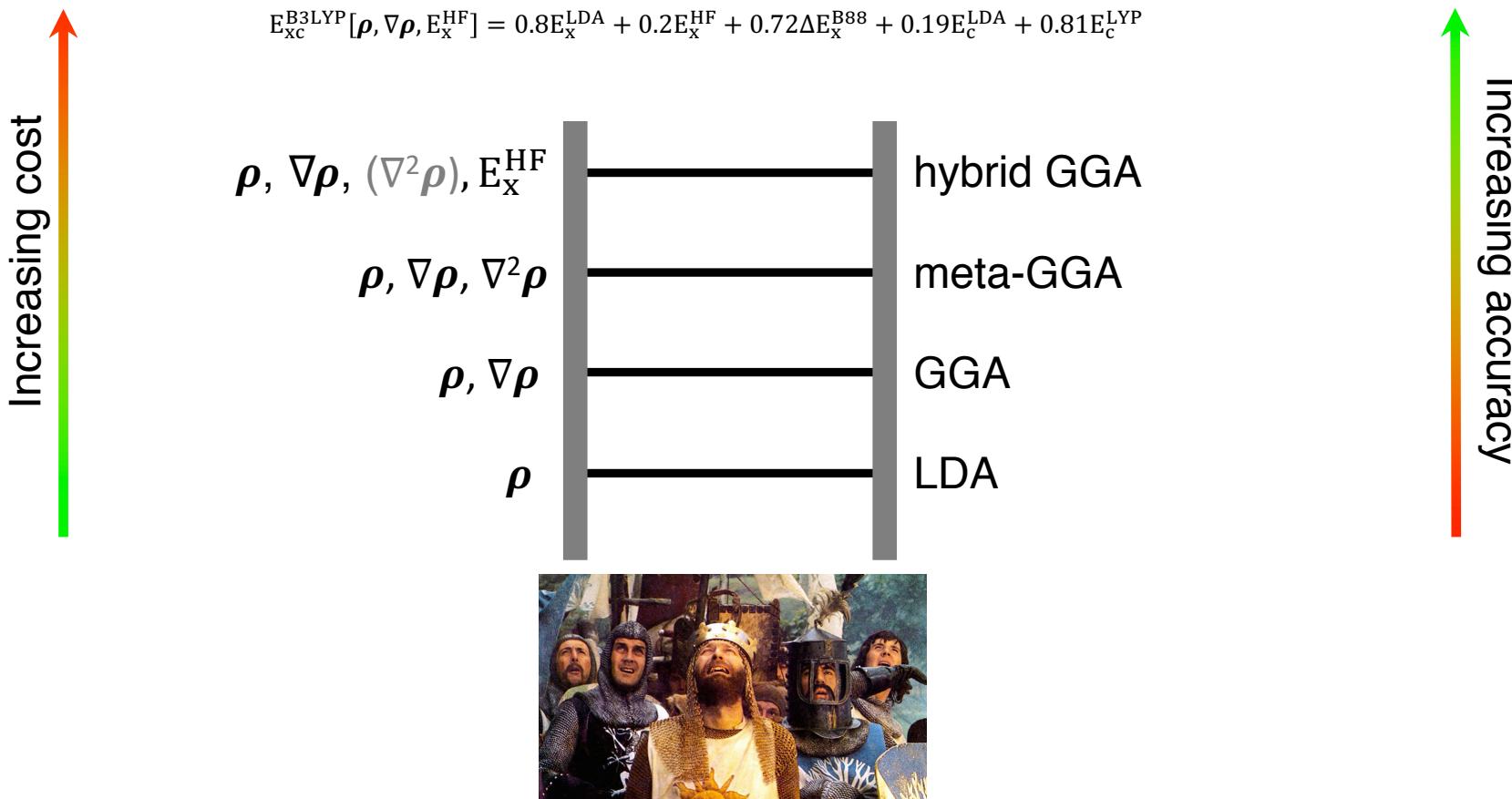
Jacob's Ladder of DFT: The Fourth Rung (Hybrid GGA)

Hybrid (meta) GGA: E_{xc} is a functional of $\rho, \nabla\rho, E_X^{\text{HF}}$ (and sometimes $\nabla^2\rho$)

Key approximation: Include exact (HF) exchange

Example: B3LYP (3 empirical parameters)

*Correction of SIE / overdelocalisation
Use adiabatic connection theorem*



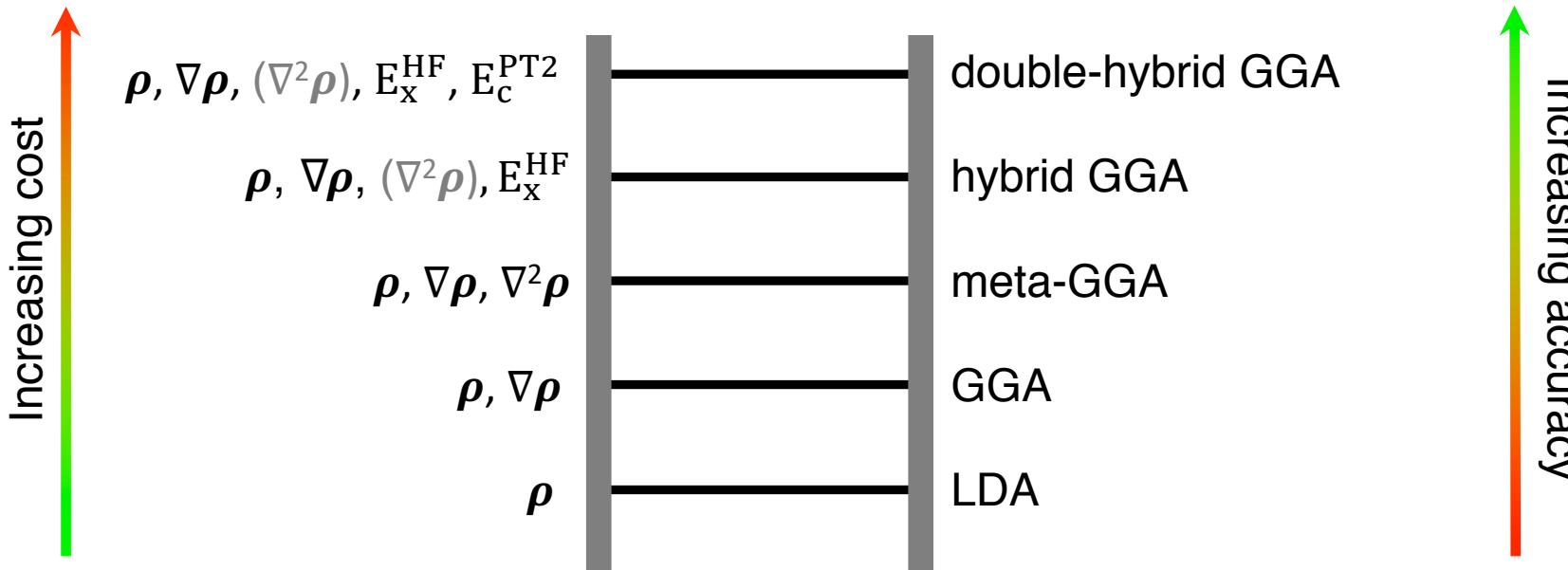
Jacob's Ladder of DFT: The Fifth Rung (Double-hybrid GGA)

Double-hybrid (meta) GGA: E_{xc} is a functional of ρ , $\nabla\rho$, E_x^{HF} , E_c^{PT2} (and sometimes $\nabla^2\rho$)

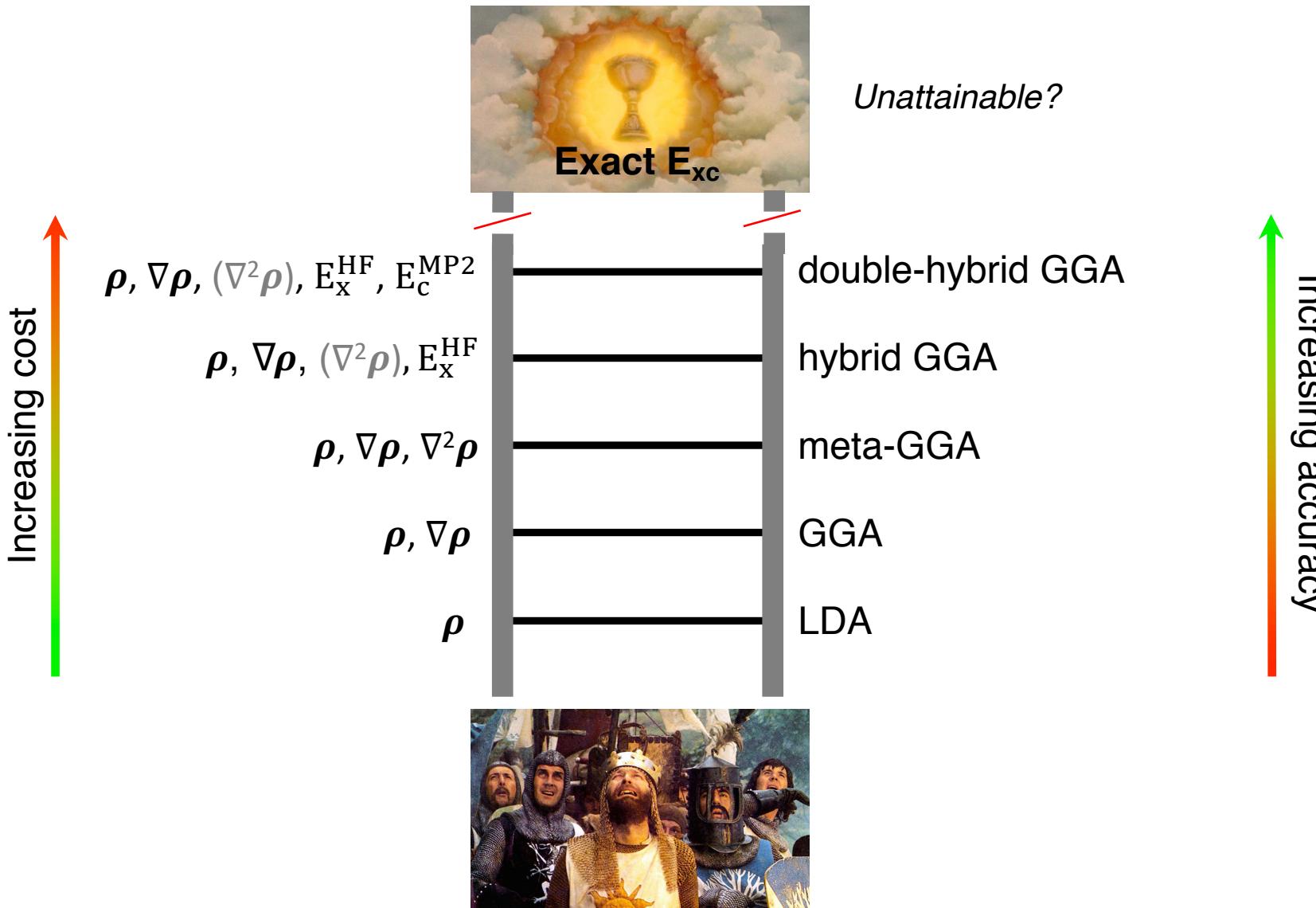
Key approximation: Inclusion of exact MP2-like correlation

Example: B2PLYP (2 empirical parameters)

$$E_{xc}^{\text{B2PLYP}}[\rho, \nabla\rho, E_x^{\text{HF}}, E_c^{\text{PT2}}] = 0.47E_x^{\text{B88}} + 0.53E_x^{\text{HF}} + 0.73E_c^{\text{LYP}} + 0.27E_c^{\text{PT2}}$$



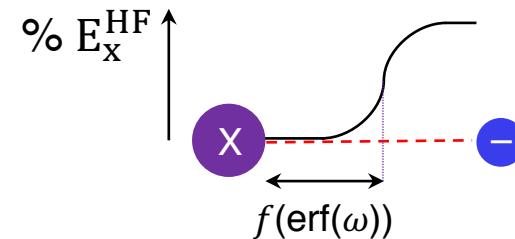
Jacob's Ladder of DFT: The Future of DFT



Shortcomings of DFT and Ways to Improve

ρ is a local property

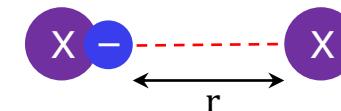
- Range-separated functionals:



e.g. $\omega\text{B97X-D3}$, CAM-B3LYP

Improves overdelocalisation and dissociation

- Dispersion corrections:



| Method | Approximation | Cost |
|--------|---|--------------|
| D3 | $\sum \frac{C_6}{r^6}$ | $\sim 0\%$ |
| D3(BJ) | C_6 depends on α and $\langle \mu^2 \rangle$ | $\sim 50\%$ |
| VV10 | Depends on ρ | $\sim 100\%$ |

Improves long-range weak interactions

Conclusions: DFT vs WFT

- In practice, DFT scales as $\sim N^4$ – same as HF, far greater accuracy
- DFT HOMO–LUMO gap \approx first excitation energy
- DFT often works better than (single reference) WFT for multireference systems

Further reading

Books

1. **Computational Chemistry** (Oxford Chemistry Primer). Harvey, J. 2018 (a good introductory text)
2. **Introduction to Computational Chemistry.** Jensen F. 2017 (3rd ed.)
3. **Essentials of Computational Chemistry: Theory and Models.** Cramer, C. J. 2004 (2nd ed.)
4. Computational Inorganic and Bioinorganic Chemistry (**Which functional should I choose?**). Rappoport, D., Crawford, N. R. M., Furche, F., Burke, K. 2008
5. **Density Functional Theory of Atoms and Molecules.** Parr. R. G. and Yang, W. 1989 (*for the keen*)

Journal Articles

1. Perspective on density functional theory. Burke, K., *J. Chem. Phys.* **2012**, *136*, 150901.
2. Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals. Mardirossian, N., Head-Gordon, M., *Mol. Phys.* **2017**, *115*, 2315.
3. Challenges for density functional theory. Cohen, A. J., Mori Sánchez, P., Yang, W., *Chem. Rev.*, **2012**, *112*, 289.
4. Density functional theory is straying from the path toward the exact functional. Medvedev, M. G., Bushmarinov, I. S., Sun, J., Perdew, J. P. and Lyssenko, K. A., *Science*, **2017**, *355*, 49.