More basics of DFT

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References for ground-state DFT

- *ABC of DFT*, by KB and Rudy Magyar, http://dft.uci.edu
- *A Primer in Density Functional Theory*, edited by C. Fiolhais et al. (Springer-Verlag, NY, 2003)
- *Density Functional Theory* , Dreizler and Gross, (Springer-Verlag, Berlin, 1990)
- *Density Functional Theory of Atoms and Molecules*, Parr and Yang (Oxford, New York, 1989)
- *A Chemist's Guide to Density Functional Theory* , Koch and Holthausen (Wiley-VCH, Weinheim,2000)

What we’ll cover

- Simplest possible example of a functional
- Essentials of KS-DFT, and functional zoo
- Important conditions not met by standard functionals: Self-interaction and derivative discontinuity
- Exact exchange
- Quiz

Atomic units and particles in box

- In atomic units, all energies are in Hartree (1 H = 27.2 eV) and all distances in Bohr (1 a_0 = 0.529 Å)
- To write formulas in atomic units, set $e^2 = \hbar = m_e = 1$
- E.g., usual formula for energy levels of infinite well of width L:

$$\varepsilon_j = \frac{h^2 j^2}{8mL^2}, \quad j = 1,2,3,\ldots$$

- Atomic units, box length L=1:

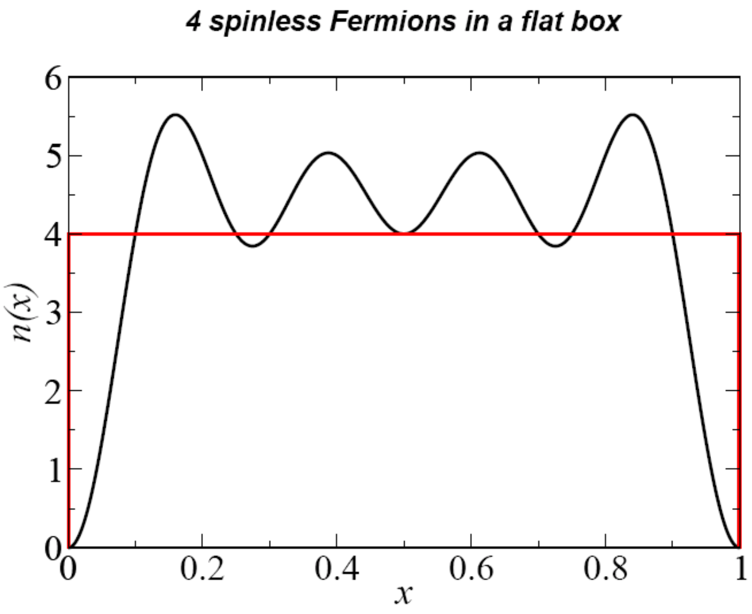
$$\varepsilon_j = \frac{\pi^2 j^2}{2}, \quad j = 1,2,3,\ldots$$

Constructing your very first density functional

- Let's look at the kinetic energy of spinless fermions in 1d: $T_s[n] = \frac{1}{2}\int_{-\infty}^{\infty} dx \sum_{j=1}^{N} \left|\frac{d\phi_j(x)}{dx}\right|^2$
- Is there some way to get T_s *without* evaluating all those damn orbitals? Yes!
- Write it as a *density* functional, i.e., an integral over some function of n(x).
- Simplest choice: a local approx:

$$T_S^{(0)}[n] = \frac{\pi^2}{6}\int_{-\infty}^{\infty} dx\, n^3(x)$$

Particles in box

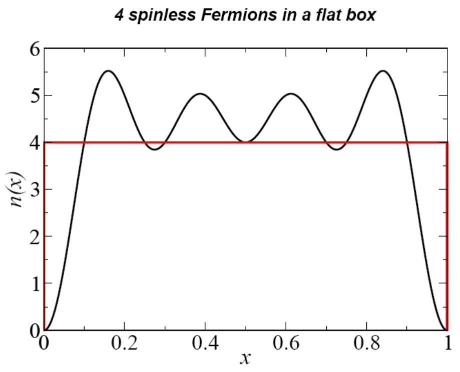


- Accuracy

N	$T_s^{[0]}$	T_s	%err
1	4.112	4.934	-17
2	21.79	24.67	-12
3	62.92	69.09	-9

What we've learned

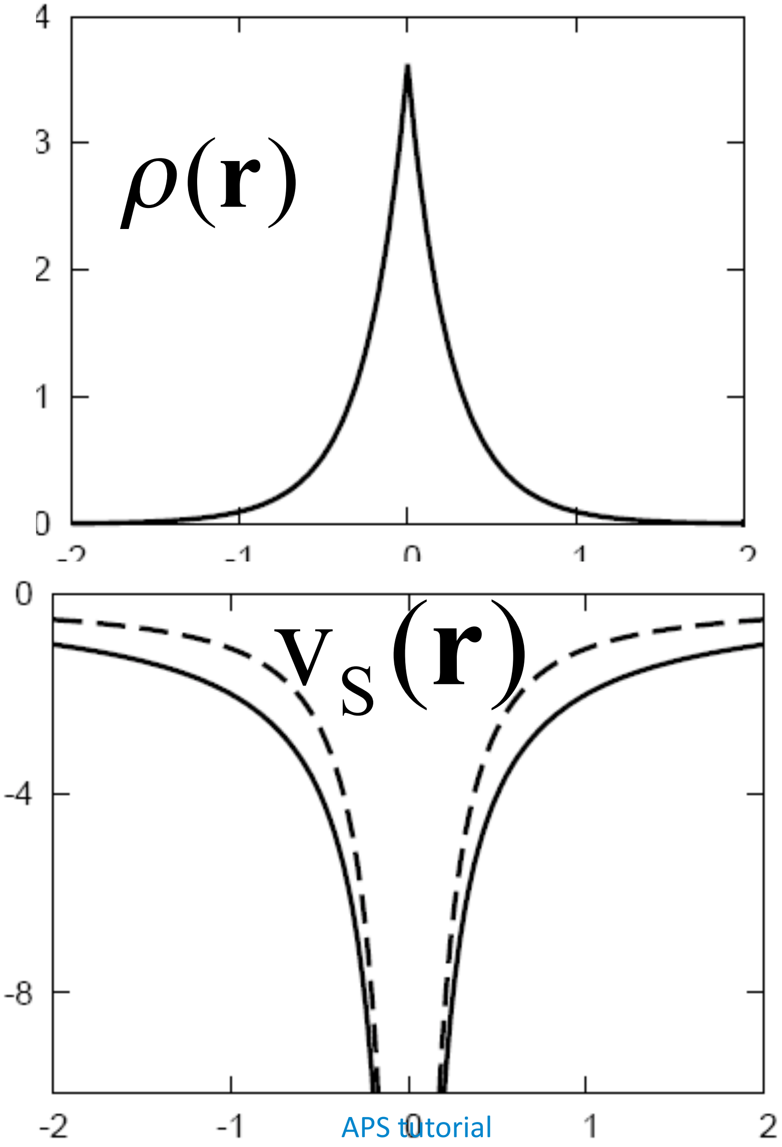
- Density functionals are approximations for the energy of many particles
- Work best for large N, worst for small N
- Local approximations are crudely correct, but miss details



Essence of Kohn-Sham DFT

- Even with exact $E_{xc}[n]$, only get E_0 and $n(\mathbf{r})$ (and I). So other properties may not be right.
- Results only as good as functional used.
- Vast amount of information from E_0 alone, such as geometries, vibrations, bond energies…
- Well-fitted functionals are accurate for limited set
- Non-empirical functionals less so, but more reliable for a broader range, and errors understandable

He atom in Kohn-Sham DFT



Everything has (at most) one KS potential

Dashed-line:

EXACT KS potential

Functionals in common use

- Local density approximation (LDA)
  - Uses only n(**r**) at a point. $E_{\mathrm{XC}}^{(0)}[n] = \int d^3r\, e_{\mathrm{XC}}^{\mathrm{unif}}(n(\mathbf{r}))$
- Generalized gradient approx (GGA)
  - Uses both n(**r**) and |∇n(**r**)| $E_{\mathrm{XC}}^{\mathrm{GGA}}[n] = \int d^3r\, e_{\mathrm{XC}}(n, |\nabla n|)$
  - More accurate, corrects overbinding of LDA
  - Examples are PBE and BLYP
- Hybrid:
  - Mixes some fraction of HF
  - Examples are B3LYP and PBE0

Functional soup

- Good: choose one functional of each kind and stick with it (e.g., LDA or PBE or B3LYP).
- Bad: Run several functionals, and pick ‘best’ answer.
- Ugly: Design your own functional with 2300 parameters.

Functional Zoology

- Empirical
  - GGA: BLYP
  - Hybrid:B3LYP
- Names:
  - B=B88 exchange
  - LYP=Lee-Yang-Parr corelation

- Non-empirical
  - GGA: PBE
  - Meta-GGA: TPSS
  - Hybrid:PBE0

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Simple conditions for Coulomb systems

- Asymptotic decay of the density

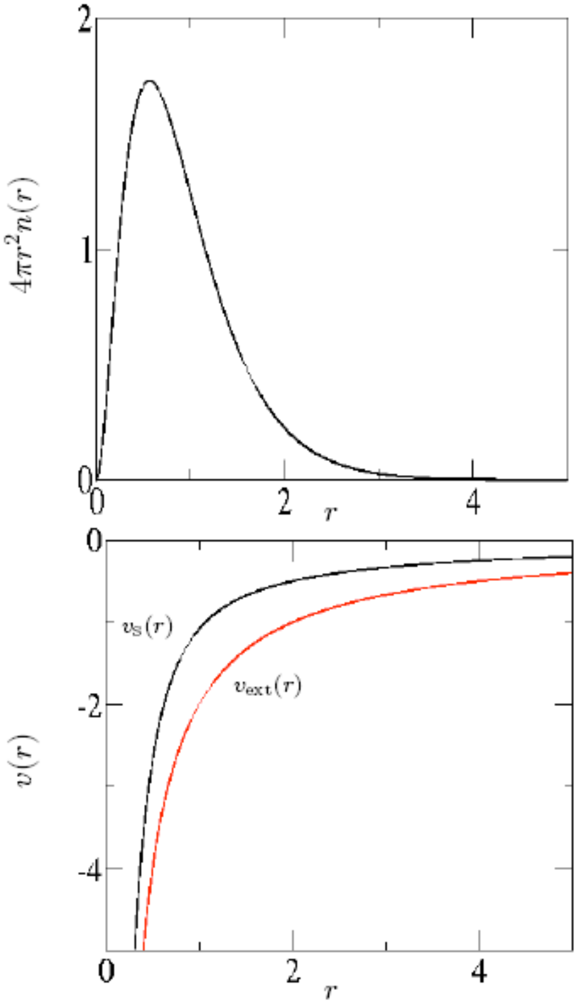
$$\sqrt{n(\mathbf{r})} \rightarrow A r^{\beta} \mathrm{e}^{-\sqrt{2I} r}$$

- Leads to severe constraint on KS potential

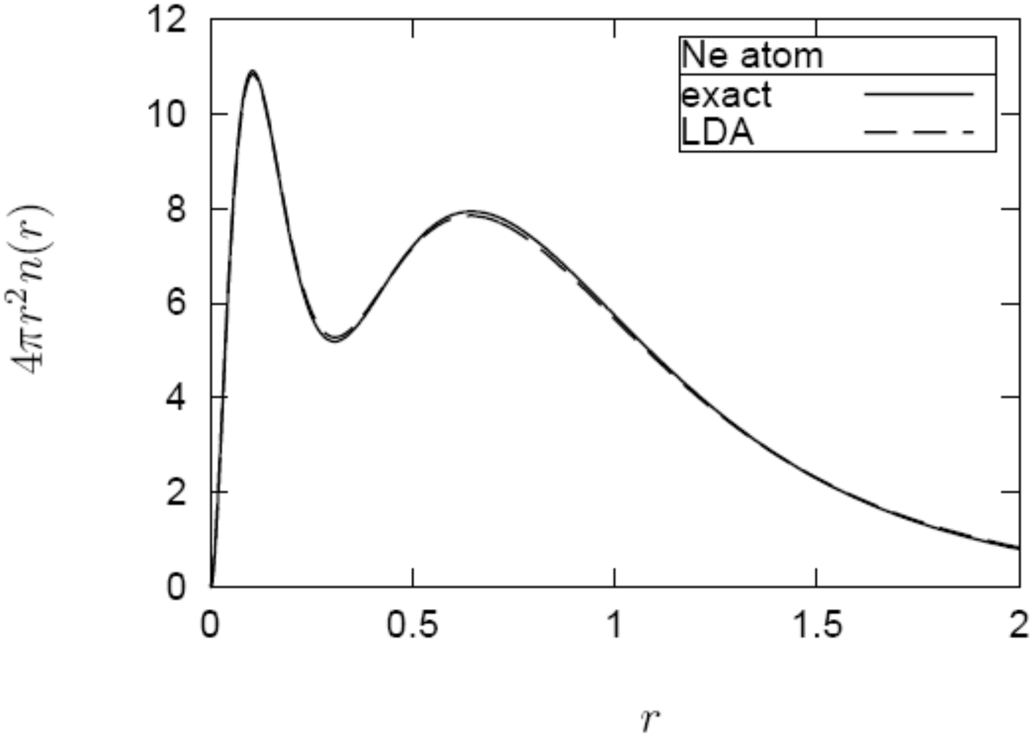
$$v_{\mathrm{xc}}(\boldsymbol{r}) \rightarrow -1/r \qquad (r \rightarrow \infty)$$

- And determines KS HOMO: $\varepsilon_{\mathrm{HOMO}} = -I$

KS potential for He atom



Densities



LDA potential

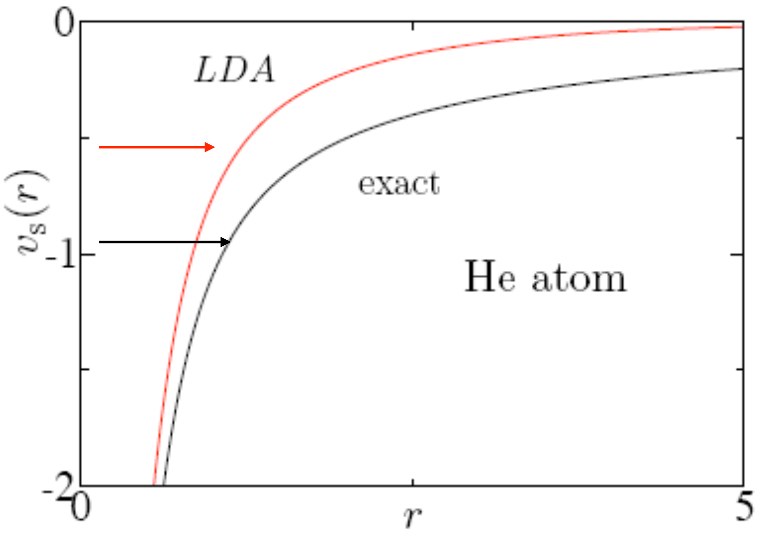
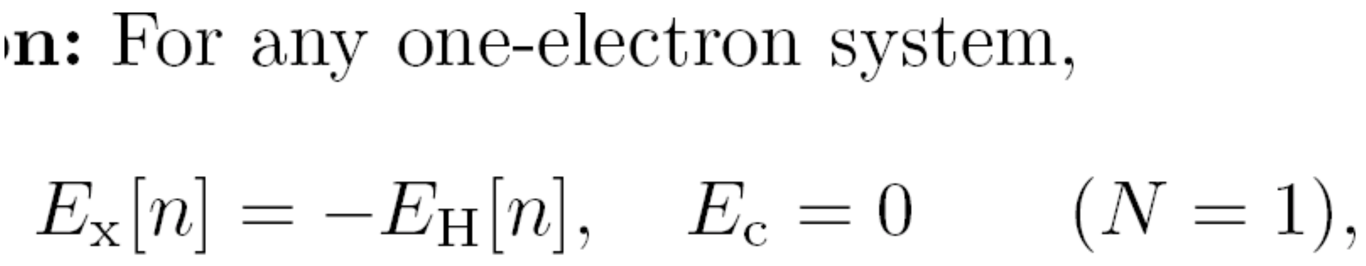


FIG. 7: Exact and LDA KS potentials for the He atom.

LDA potential for the He atom. It decays far too rapidly, and so its orbitals are far too shallow. The HOMO is at -0.5704 H, while the LUMO is not bound at all.

Self interaction

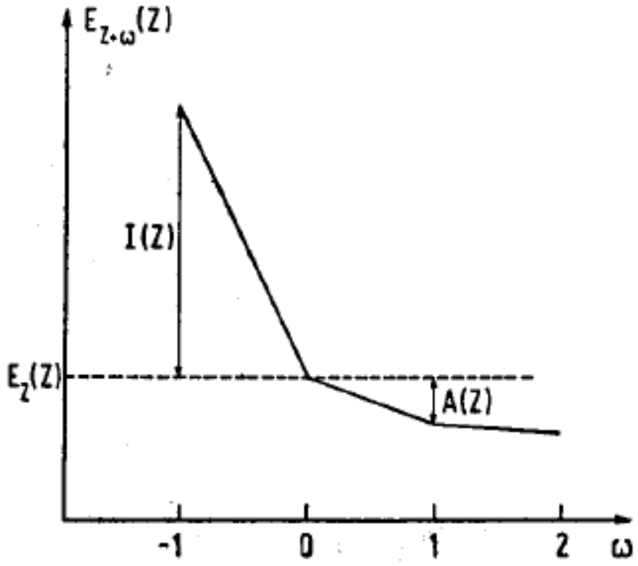
- Violated by most semilocal functionals (unless built in)



n: For any one-electron system,

$$E_{\mathrm{x}}[n] = -E_{\mathrm{H}}[n], \quad E_{\mathrm{c}} = 0 \qquad (N = 1),$$

Energy as function of N

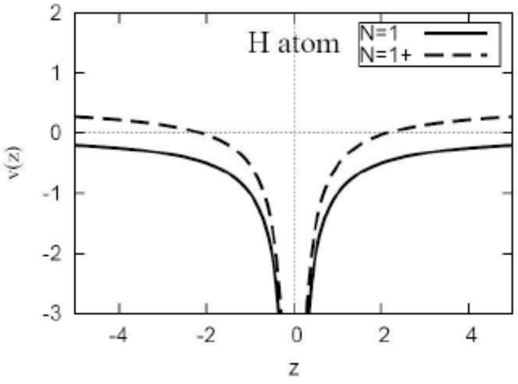


From Dreizler + Gross

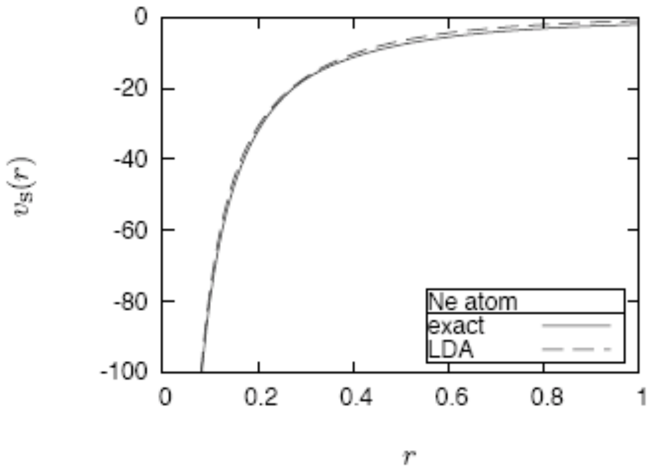
Fig. 2.2. Ground state energy of an atom with nuclear charge Z and $(Z+\omega)$ electrons

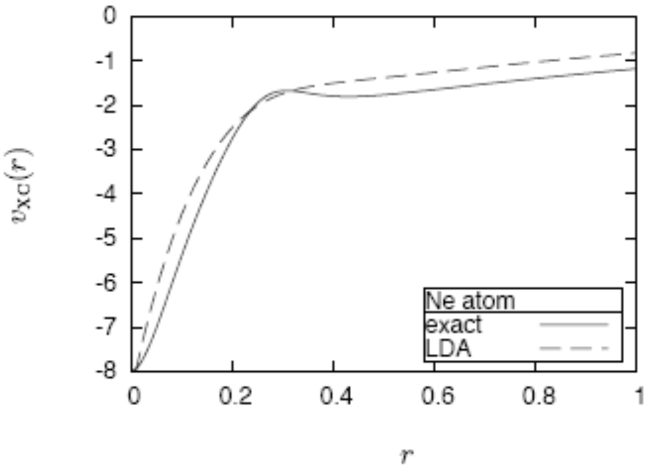
Derivative discontinuity

- When you add a tiny fraction of an electron to a system, the KS potential shifts uniformly, since before, ε_{HOMO} (N)=-I, but now, ε_{HOMO} (N+δ)=-A
- Thus $v_s(r)$ must jump by Δ_{xc}=(I-A)- (ε_{HOMO}-ε_{LUMO})



Ne Potentials

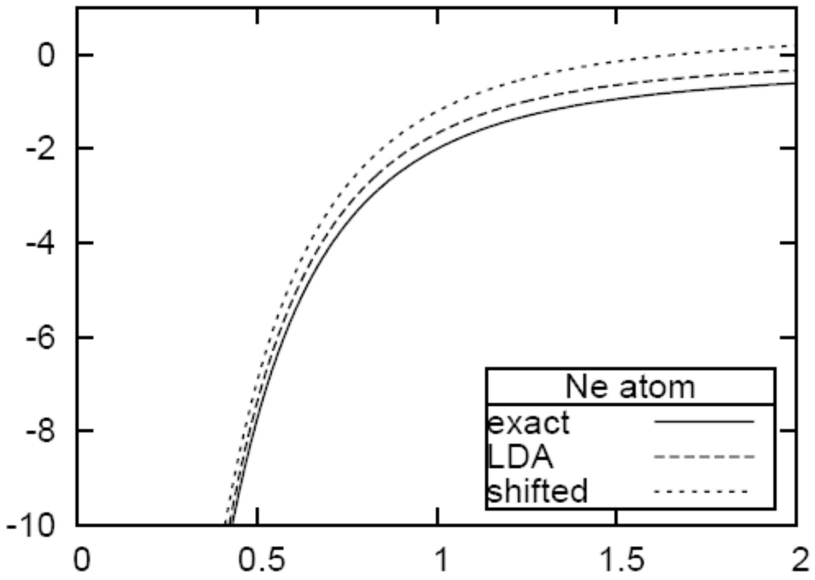




$$v_{\mathrm{XC}}(\boldsymbol{r}) \to -1/r \qquad (r \to \infty)$$

$$\varepsilon_{\mathrm{HOMO}} = -I$$

Missing derivative discontinuity in LDA



LDA looks like exact, shifted by about I/2

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What ever happened to HF?

- We know E_x is just

$$-\frac{1}{2}\sum_{\sigma}\sum_{\substack{i,j\\ occ}}\int d^3r\int d^3r'\,\phi^*_{i\sigma}(\mathbf{r})\,\phi^*_{j\sigma}(\mathbf{r}')\,\phi_{i\sigma}(\mathbf{r}')\,\phi_{j\sigma}(\mathbf{r})/|\mathbf{r}-\mathbf{r}'|$$

- So why can’t we just put that in KS equations?

- Because don’t know $E_x[n]$, so must approximate

OEP

See RMP , Kuemmel and Kronik

- Way to handle orbital-dependent functionals in KS scheme, i.e., with single multiplicative KS potential
- Still density functionals, since orbitals uniquely determined by density
- Often called OPM
- Several schemes to implement, all much more expensive than regular KS-DFT
- Can improve other properties:
  - No self-interaction error
  - Potentials and orbital energies much better
  - Approximates derivative discontinuity

HF versus EXX

- HF minimizes E_x $[\{\phi_i\}]$ over all possible wavefunctions
- EXX includes additional constraint of common potential (i.e., KS)
- Yield almost identical total energies, with HF an eensty bit lower.
- Occupied orbital energies very similar, but big difference in unoccupied orbitals

A tale of three gaps

- Fundamental gap:
  - $\Delta = I - A$ =24.6eV for He
- Kohn-Sham gap:
  - $\Delta_s = \varepsilon_{HOMO} - \varepsilon_{LUMO}$ = 21.16 eV
- Derivative discontinuity: $\Delta_{xc} = \Delta - \Delta_s$
- Lowest optical transition:
  - $\omega_{min} = E(1s,2p) - E(1s^2)$ = 21.22eV
- NOTE: All same if non-interacting, all different when interacting
- Of course, ε_{HOMO}(LDA)=15.5 eV

Quiz

1. Do local functionals do better for:

   A. small N, B. large N ?

2. How many empirical parameters are too many?

   A. 1; B. 10., C. 100+

3. GGA's have no self-interaction error,

   True or false?

4. The Kohn-Sham gap would equal the true gap if only we had the exact functional?
5. Why not use E_x in small calculations to improve geometries, etc.?

What we've learned, maybe

- Ground-state density determines all properties of system, *in principle*, but in practice, only really get energy and density (which is 90% of what you want).
- Local density functional theories give roughly correct answers, but are too inaccurate to be helpful in quantum chemistry.
- The commonly-used functionals in chemistry are well-founded and have few parameters.
- There are known exact properties of the density in real atoms.
- There are subtle and bizarre effects in the KS potential because real electrons do interact.
- Exact exchange is expensive, and we don't have a correlation functional to go with it, but it improves some properties.