More basics of DFT

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References for ground-state DFT


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:

\[ \varepsilon_j = \frac{\hbar^2 j^2}{8mL^2}, \quad j = 1,2,3,... \]

• Atomic units, box length L=1:

\[ \varepsilon_j = \frac{\pi^2 j^2}{2}, \quad j = 1,2,3,... \]
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 \( T_s \) \textit{without} evaluating all those damn orbitals? Yes!

• Write it as a \textit{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

<table>
<thead>
<tr>
<th>N</th>
<th>$T_s^{[0]}$</th>
<th>$T_s$</th>
<th>%err</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>4.112</td>
<td>4.934</td>
<td>-17</td>
</tr>
<tr>
<td>2</td>
<td>21.79</td>
<td>24.67</td>
<td>-12</td>
</tr>
<tr>
<td>3</td>
<td>62.92</td>
<td>69.09</td>
<td>-9</td>
</tr>
</tbody>
</table>
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 $n(r)$ (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

\[ \rho(r) \]

\[ V_s(r) \]

Dashed-line: EXACT KS potential
Functionals in common use

• Local density approximation (LDA)
  — Uses only $n(r)$ at a point.
  
  \[ E_{XC}^{(0)}[n] = \int d^3 r \, e_{XC}^{\text{unif}}(n(r)) \]

• Generalized gradient approx (GGA)
  — Uses both $n(r)$ and $|\nabla n(r)|$
  — 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 correlation

• Non-empirical
  – GGA: PBE
  – Meta-GGA: TPSS
  – Hybrid:PBEO
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Simple conditions for Coulomb systems

• Asymptotic decay of the density

\[ \sqrt{n(r)} \rightarrow Ar^\beta e^{-\sqrt{2I}r} \]

• Leads to severe constraint on KS potential

\[ v_{xc}(r) \rightarrow -1/r \quad (r \rightarrow \infty) \]

• And determines KS HOMO:

\[ \varepsilon_{\text{HOMO}} = -I \]
KS potential for He atom
Densities

\[4\pi r^2 n(r)\]

\(r\)
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.

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

- Violated by most semilocal functionals (unless built in)

\[ E_X[n] = -E_H[n], \quad E_c = 0 \quad (N = 1), \]
Energy as function of $N$

![Graph](Image)

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

From Dreizler + Gross
**Derivative discontinuity**

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

\[ v_{xc}(r) \rightarrow -\frac{1}{r} \quad (r \rightarrow \infty) \]

\[ \varepsilon_{\text{HOMO}} = -I \]
Missing derivative discontinuity in LDA

LDA looks like exact, shifted by about 1/2

APS tutorial
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What ever happened to HF?

• We know $E_x$ is just

$$\frac{-1}{2} \sum_{\sigma} \sum_{i,j} \int d^3r \int d^3r' \phi_i^\sigma(r) \phi_i^\sigma(r') \phi_j^\sigma(r') \phi_j^\sigma(r')/|r - r'|$$

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

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

OEP

See RMP, Kuemmel and Kronik
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 eensy bit lower.

• Occupied orbital energies very similar, but big difference in unoccupied orbitals
A tale of three gaps

• Fundamental gap:
  – \( \Delta = I - A \) = 24.6 eV for He

• Kohn-Sham gap:
  – \( \Delta_s = \varepsilon_{HOMO} - \varepsilon_{LUMO} = 21.16 \text{ eV} \)

• Derivative discontinuity: \( \Delta_{xc} = \Delta - \Delta_s \)

• Lowest optical transition:
  – \( \omega_{min} = E(1s,2p) - E(1s^2) = 21.22 \text{ eV} \)

• NOTE: All same if non-interacting, all different when interacting
• Of course, \( \varepsilon_{HOMO}(LDA) = 15.5 \text{ eV} \)
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.