Open questions in DFT

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Santiago, 2011
What can an independent particle Hamiltonian tell about an interacting particle Hamiltonian?
Introduction
Impact of DFT

Web of Science: "density functional theory"

\[
\log_{10}(\text{citations})
\]

Year: 197*, 198*, 199*, 200*, 2050*
Why this talk?

1989, 10th Canadian Symposium on Theoretical Chemistry

John Pople: Why is $H_2^+$ not working?

Axel Becke: Take another method for $H_2^+$!

A. Becke showed with systematic tests that DFAs work well.

J. Pople became an adept of DFT
Introduction

**H$_2^+$ problem**

![Graph showing the $H_2^+$ problem with LDA approximation versus exact results.](image)
Some papers on $\text{H}_2^+$, et al.

1992
R. Merkle et al., JCP 97, 9216 (1992):

$X_2^+$ molecules

1998

3-e bonds
Some people still interested in this problem

Citations of paper by Braïda et al. : ε

Negative results not published or publication irrelevant?
Overview

- Is accurate DFT accessible?
- Are systematic constructions of DFAs accessible?
- What should be approximated?
- Is degeneracy correctly described?
- Are statistics relevant?
Is accurate DFT accessible?

DFT is exact. Can we approach it numerically?

Accurate DFT is difficult to reach and this is done in an uncontrolled way.
Accurate DFT?

DFT and DFAs

- D: density
- F: functional
- T: theory
- A: approximations

X: "DFT is not working"

M. Levy: "Is DFT not working or the approximation?"
Accurate DFT?

T in DFT

- Wave function theory:

\[ E_0[\nu] = \min_{\Psi} \langle \Psi | T + V + V_{ee} | \Psi \rangle \]

\[ V = \sum_{i=1,N} \nu(r_i) \]

- DFT (Hohenberg-Kohn / E. Lieb):

\[ F[n] = \max_{\nu}(E_0[\nu] - \int \nu n) \]

\[ E_0[\nu] = \min_{n}(F[n] + \int \nu n) \]
"$F[n]$ is unfortunately unknown"

$F[n]$ is known, $= \max_v (E_0[v] - \int v \, n)$

Example: $n = N \frac{1}{\pi} e^{-2r}$

<table>
<thead>
<tr>
<th>$N$</th>
<th>1</th>
<th>2</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F[n]$</td>
<td>0.5</td>
<td>1.588</td>
<td>6.827</td>
</tr>
</tbody>
</table>

F. Colonna, AS, JCP110, 2828 (1999)
See also: Teale, Coriani, Helgaker

More difficult to calculate than $\min_{\Psi} \langle \Psi \mid H \mid \Psi \rangle$
Accurate DFT?

Is $v$ accessible?

$$F[n] = \max_v (E_0[v] - \int v \, n)$$

J.E. Harriman (~1980’s):

HK theorem not valid in a finite basis
Is $v$ accessible for the H atom in a finite basis?

Basis: 1s, 2s

\[ v = -1/r + \Delta v \]

\[ \Delta v = \frac{12256213732454395368}{72539740899199421} e^{-4r} + \frac{4658295494941200000}{72539740899199421} e^{-3r} (2 - 2r) + \frac{1179894519818100000}{72539740899199421} e^{-2r} (2 - 2r)^2 \]

makes 1s and 2s degenerate (in this space):

1s is an acceptable solution.
Is $\nu$ accessible for the H atom in a finite basis?

H atom, corrections to $\nu = -1/r$, making the orbitals degenerate, for small basis sets.
Is $\nu$ accessible for Kohn-Sham?

Kohn-Sham defines:

$$F[n] \rightarrow T_s[n] = \max_{\nu} (E_0, V_{ee} \rightarrow 0[\nu] - \int \nu \, n)$$

$$\nu_{KS} = \nu_{\text{max}}$$

Success of KS

$\leftarrow$ fast calculation for non-interacting particles

$$(T + V_{KS}) \Psi_{KS} = E_{KS} \Psi_{KS}$$
Accurate DFT?

\[ \Delta \nu(r) \text{ making } \Psi_{\text{FCI}} = \Psi_{\text{KS}} = \Psi_{\text{OEP}} \]

... for He atom, VDZ basis (via orbital degeneracy)

D. Rohr, AS (2010)
Accurate DFT?

Conclusion

• $F[n]$ : second-order errors

• $v_{KS}(n)$, ...: ?

..., ..., E. Lieb
Are systematic constructions of DFAs accessible?

DFAs - semi-local.

How to overcome this?

Systematic constructions of DFAs are not known.
Construction of approximations

\[ \mathcal{F}[n] \approx \int f([n(r), |\nabla n(r)|, ...] ) d^3 r \]
Available approximations

• LDA

• GGAs, m-GGAs, ...

• Hybrids: B3LYP, ...

• ...

Quite limited ansatz
DFA construction?

Quite limited ansatz. Example

\[ E_n[n] = \frac{1}{2} \int \int n(r_1) n(r_2) / |r_1 - r_2| \]
\[ \approx \int f[n(r), |\nabla n(r)|, ...] d^3 r \]

\( E_n[n] \) is known.

Is a (semi-)local approximation working?

E. Cancès’ answer
Behavior of $U$ at $\infty$ separation

\[ n = n_A \ldots n_B \]

\[ E_h = \ldots + \frac{1}{2} \int n_A(r) n_B(r') / |r - r'| \]

\[ E_h \rightarrow \ldots + \frac{1}{2} N_A N_B / |R_A - R_B| \]
Conclusion

- From $n \Rightarrow$ explicit dependence on $R_{AB}$?

  ($E_h[n]$, but also van der Waals interaction,...)
What should be approximated?

Not $F[n]$ is approximated, but a part of it.

There is no ideal choice for the part of $F[n]$ to approximate.
Hohenberg-Kohn

\[ F[n] = E_h[n] + E_{kxc}[n] \]

\[ E_h[n] \equiv \frac{1}{2} \int \int d^3 r_1 d^3 r_2 n(r_1) n(r_2) / r_{12} \]

\[ E_{kxc}[n] \text{ defined above, by choice of } E_h \]

Motivation: electrostatics right
(as are \( \int \nu_{ne} n, \nu_{nn} \))

cf. Madelung potential, semi-empirical methods,
W. Kutzelnigg on dipole moments...,
Kohn-Sham

\[ F[n] = E_h[n] + T_s[n] + E_{xc}[n] \]

\[ T_s[n] = \min_{\Psi \to n} \langle \Psi | T | \Psi \rangle \]

\[ E_{xc}[n] \text{ defined above, by } F[n], E_h[n], T_s[n] \]

Motivation:
Pauli principle (repulsion) mainly in \langle T \rangle
Approximate what?

Kohn-Sham (b)

\[ F[n] = E_h[n] + T_s[n] + E_x[n] + E_c[n] \]

\[ E_x[n] = \langle \Psi_{\text{min}},\rightarrow | V_{\text{ee}} | \Psi_{\text{min}},\rightarrow \rangle - E_h[n] \]

\[ E_c[n] \text{ defined above} \]

Motivation: a smaller part to approximate
A term remains to be approximated

Hope:

approximations work better for remaining term
Example: one-electron systems

no e-e repulsion

\[ E_h[n] + E_{xc}[n] = 0, \text{ or } E_{xc}[n] = -E_h[n] \]

If we cannot approximate \( E_h[n] \),

how can we approximate \( E_{xc}[n] \)?

cf. \( \text{H}_2^+ \) problem

R. Merkle et al., JCP 97, 9216 (1992)
Conclusion

• Problems avoidable?

- electrostatics: separate $E_h$!

- self-interaction: $E_h + E_{xc}$!
Is degeneracy correctly described?

Degeneracies are commonly observed.

With DFAs we do not known how to deal with degeneracies.
Degeneracy in DFAs

\[ F[n_i] = \text{const, } \forall \; n_i \in \text{degenerate set} \]

- “\(N\)-conserving”
- “\(non \; N\)-conserving”

Using spin-density amplifies the problem
Example of \( N \)-conserving degeneracy

\[
E(B, \ ... + \frac{1}{2} (p_x^2 + p_y^2)) = E(B, \ ... + p_x^2)
\]
Degeneracy?

Example of non $N$-conserving degeneracy

- Dissociated $\text{H}_2^+$

\[ E(\text{H}_2^+, R \to \infty) = 2 \, E(\text{"H}^{1/2}\text{"}) = E(\text{H}) + E(\text{H}^+) \]

\[ n_A \ldots n_B = \sigma_g^2 \to \frac{1}{2} \, n_A + \frac{1}{2} \, n_B \]
Degeneracy?

How important are density changes?

N₂  HCCCH

X-ray, e.g., SrSi

Chemical Bonding
Spin-density in DFAs

For DFAs

\[ F[n] \rightarrow F\left[n = n_\alpha + n_\beta, m = n_\alpha - n_\beta\right] \]

Theory, parallels \( F[n] \), adding “magnetic field”.

\( m \neq 0 \Rightarrow \text{degenerate states, when } B = 0. \)

Thus, \( F[n, m] \) should be independent of \( m \).

DFAs for \( F[n, m] \) deliberately \( m \)-dependent.
Why care about degeneracy?

Can we choose among degenerate states, e.g., choose maximal $|m|$?

Not always free: degeneracy can be lifted (approached) in a specific way, e.g., for potential energy surfaces (chemical reactions, adsorption, ...).
Degeneracy?

Potential energy curve for $H_2$, LDA

Restricted and Unrestricted Kohn-Sham (RKS, UKS)

Choice:

- right $m$ (RKS)

- $\approx$right $E$ (UKS), right $M_S = \frac{1}{2} \int m = \frac{1}{2} (N_\alpha - N_\beta)$
Degeneracy?

\( \text{O}_2 \left( ^3\Sigma \right) \ R \to \infty : M_S \ (\text{or } N_\alpha, N_\beta) \text{ not conserved} \)

\( \text{O}_2: \) triplet, \( M_S = 1 \)

Size-consistency requires:

\( \text{O}(\uparrow \uparrow) \ldots \text{O}(\uparrow \uparrow) \Rightarrow M_S = 2, \text{ not } 1 \)

\( \text{O}(\uparrow \uparrow) \ldots \text{O}(\downarrow \downarrow) \Rightarrow M_S = 0, \text{ not } 1 \)

\( N_\alpha, N_\beta = ? \) What Slater determinant?
O$_2$ (\( ^3\Sigma \)) $R \rightarrow \infty$ : "phase transition"

For $R_e$, ground state has $M_S = 1$.

For large $R$, in DFAs

\[ E(M_S = 0 \text{ or } 2) < E(M_S = 1) \]

- "phase transition"
Degeneracy?

Conclusion

DF is

• sensitive to small $\Delta n$, to describe binding
• insensitive to large $\Delta n$, to describe degeneracy

How can this be realized with a DFA?

Degeneracy $\leftarrow$ external potential, not $n$

Problem for parts of $F[n]$ even more complicated (supplement)
Functionals trained, judged by test sets.

Statistics on test sets need care.

Statistics are not applicable for particular cases.
Statistics relevant?

Strategy

Test sets

• statistics
→ general idea of the quality of the DFA

• grouping of data
→ when to use it, and when not

DFAs: 'good'
For those who are in a hurry to get good results

Scientifically indisputable:
no hiding of bad results

No need for new
• parametrizations
• calculations

Example:
better three electron bonding energies (He$_2^+$, ...
Errors in dissociation energies for $X_2^+$

ΔE (kcal/mol)

Statistics relevant?

Explanation: how not to group results

set 1, set 2
Statistics relevant?

Explanation: how to group results

set 1, set 2
How to judge the relevance of test sets?

Do statistics help in a particular case?
I know what *must* be,
but I do not know what *may* be
Idries Shas, *The Pleasantries of Mulla Nasrudin*

- Accurate DFT: accessible, but difficult to reach
  and in an uncotrolled way

- Systematic constructions of DFAs: not known

- Part of $F[n]$ to approximate: no ideal choice

- DFAs when degeneracies occur: not known

- Statistics on test sets: need care
“... el mas importante...
Que sólo vuela el que se atreve al hacerlo”

“... the most important...
That only flies the one who dares to do it”