Dealing with spatial regions

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Questions, no answers
Overview

- Why & why it is difficult
- ’Atoms’ in DFT integration
- Non-atomic domains
- More complicated shapes
- Variable shape
- Further problems
Structure

- A chemical example
- A mathematical example
- A realistic example
- Conclusion
Regional treatment: Why & why it is difficult
A chemical example

Regions in molecules

Atoms in caffeine
A mathematical example

Integration on a subdomain

Gaussian points on $[0, 1]$, integration on $[0, x_0]$
A realistic example

Shape optimization

Region having maximal probability to find a pair of electrons (CH$_4$)

Conclusion

Where the problem is

- 3D

- Regions where the integrand changes rapidly inside the integration domain: large number of points for accuracy

- Changes at the border of the integration domain are more important (differences, optimization,..)

- Function to optimize may depend on integration domain
Conclusion

Where the problem is

\[
\int_{x_0}^{x_0} f
\]
Comment

Problem in DFT

• Solved (?)

• $O(N)$
’Atoms’ in DFT integration

- The idea: cells

- Smooth cells
The idea

**D: electron density, \( \rho (r) \)**

\( \rho(x, y) \)
The idea

F: functional of the density, $\int f(\rho(r), \ldots)$

$f(\rho(x, y))$
The idea

Partitioning the integrand

\[ \sum_i w_i(r) = 1 \]

\[ f(r) = (\sum_i w_i(r)) f(r) = \sum_i f_i(r) ; \quad f_i(r) = w_i(r) f(r) \]

\[ \int f(r) = \sum_i \int f_i(r) \]

Hopefully \( \int f_i \) easier

Boys and Rajagopal (1965), Becke (1988),...
The idea

**A spatial partitioning:** \( w_i \) scaled nearest points
Smooth cells

Deformed atoms: edges, corners, ‘bad’ partitioning
Cells: empty space

No $\sum_i w_i = 1$
Smooth cells

Smoothing of cells

some memory of the problems ...
Smooth cells

Integration: spherical coordinates
Conclusion

Gaussian integration/region

Good enough for cell?
Non-atomic domains
A chemical example

Periodic properties, shell structure
A mathematical example

Gaussian points miss change of regime
A realistic example

The correlation energy in DFT

\[ E_c \equiv E - \langle \Phi_{KS} | H | \Phi_{KS} \rangle = \int \rho(r) \varepsilon_c(r) \, d^3 r \]

\( \varepsilon_c \): not unique, but if known ...
A realistic example

How to get an accurate $\varepsilon_c(r)$ for the Be atom


$$
\varepsilon_c(r_1) = \frac{1}{2} \frac{1}{\rho(r_1)} \int d^3 r_2 \int d \lambda \left[ P_2(r_1, r_2; \lambda) - P_2(r_1, r_2; \lambda = 0) \right] / r_{12}
$$
A realistic example

$\rho(r)$, for the Be atom

Sudden changes
A realistic example

Accurate $\varepsilon_c(r)$ for the Be atom

Sudden changes
A realistic example

The integrand for $E_c(\text{Be})$: $\rho(r) \, \varepsilon_c(r)$

Sudden changes
Conclusion

The regions for integration

Grid adapted?
More complicated shapes
A chemical example

Bonds in caffeine

Regions corresponding to bonds?
A mathematical example

Unconventional borders
A realistic example

LiH...HF
Conclusion

How to integrate?

Not $\approx$ spherically symmetric
Variable shape
A chemical example

Chemical reactions

Significant changes of the bonding region
A mathematical example

**Funciton/derivatives**

\[ f(x, p), \ |\partial_x f(x, p)|, \ |\partial_p f(x, p)|, \text{ as functions of } x \]
A mathematical example

Fixed/moving points

Gauss–Hermite integration, $f = f_1 + f_2$; $f_i(x) = e^{-(x-x_i)^2}$
A realistic example

Domain obtained by optimization
Conclusion

Consistent quality of integration

Regional decomposition helps.

Good enough (shape changes with evolution)?
Further problems

- Sparse data (Quantum Monte Carlo)
- Differential equation (Overhauser model)
- 6D
Sparse data

Quantum Monte Carlo data

Region having maximal probability to find a pair of electrons (CH₄)
Differential equation

Overhauser model

model $v_{\text{eff}}(u)$ for \[ (-\frac{1}{2} \frac{d^2}{du^2} + v_{\text{eff}}(u)) \psi(u) = \mathcal{E} \psi(u) \]

$\psi(u)^2 \rightarrow f(u)$; probability to find 2 electrons at $u$

P. Gori–Giorgi, J. Perdew, PRB 64, 155102 (2001)
Quality of the Overhauser model

Extension of the Overhauser model

More than 2 electrons

Decompose into regions?
Summary

Regions reflect chemistry.

Optimism about the use regional information:

- DFT
- Chemical bonding
Conclusion

Efficient integration over arbitrary regions in 3D?

Competition with fitting functions?

Algorithms to optimize the regions?

\[ f(\ldots, \int_{\Omega} \varphi_i(r) \varphi_j(r) \, d^3 r, \ldots) \]