Information Carriers and Information Theory in Quantum Chemistry
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Quantum Chemistry

Information Carriers (3)

- Wave function $\Psi$
- Electron Density $\rho$
- Shape function $\sigma$

Reading The Information

How to “read” information content, or its difference between two systems A and B

Construction of a functional $F_{AB} = F[3_A, 3_B]$

Use of Information Theory

Case Studies

I Quantum Similarity of atoms
II Dissimilarity of enantiomers
III Information Theory in reactions: information profiles
From Conventional (= wave function) Quantum chemistry to Density Functional Theory

\[ H\Psi = E\Psi \rightarrow \Psi \rightarrow \text{properties, e.g. } \rho(r) \]

\[ \rightarrow E \quad \uparrow \]

Electron density function

N-electron system

\[ \rho(r) = N \int \Psi^*(x_1, x_2, \ldots, x_N)\Psi(x_1, x_2, \ldots, x_N) dx_1 dx_2 \ldots dx_N \]

Integration over 4N-3 variables!

- **Density Functional Theory**: \( \rho(r) \) contains all ground-state information of the atom or molecule

- No need for an “overcomplicated” wave function containing too much information.

Fundamentals and "Computational" DFT
Fundamentals of DFT


First Theorem

The external potential (i.e. due to the nuclei): $Z_A$, $R_A \forall A$

$\rho(r) \rightarrow v(r) \rightarrow \psi \rightarrow E = E[\rho(r)]$

$\rho(r)$ as basic variable

"The external potential $v(r)$ is determined, within a trivial additive constant, by the electron density $\rho(r)$"
No two different $v(r)$ generate same $\rho(r)$ for ground state

Second Theorem
- For a trial density $\tilde{\rho}(r)$, such that $\tilde{\rho}(r) \geq 0 \forall r$ and $\int \tilde{\rho}(r) \, dr = N$
- $E_0 \leq E[\tilde{\rho}]$
- $\uparrow$
- exact ground state energy

- what is $E[\rho]$ ?? : energy functional
- how can we obtain $\rho$ directly from the knowledge of $E[\rho]$?
Computational DFT

Variational procedure $\rightarrow$ Normalization of $\rho(r)$ (Lagrangian multiplier($\mu$))

$$\frac{\delta F_{\text{HK}}}{\delta \rho(r)} + v(r) = \mu \quad \rightarrow \text{Euler equation}$$

- DFT analogue of Schrödinger’s time independent equation $H\Psi = E\Psi$
- $\rho$ should be so that lefthand site of the Euler equation is a constant

Practical Implementation: Kohn Sham equations

DFT as a computational method of ever increasing importance

(Chemical Abstracts: 2007: 13000 papers)
• **Conceptual DFT**

  Parr's landmark paper on the identification of $\mu$ as (the opposite of) the electronegativity


  - Chemical reaction involves perturbation of a system in $v(r)$ and/or $N$

  Consider

  $$
  E = E[N, v(r)]
  $$

  $$
  dE = \left( \frac{\partial E}{\partial N} \right)_{v(r)} dN + \int \left( \frac{\delta E}{\delta v(r)} \right)_{N} \delta v(r) d\tau
  $$

  As

  $$
  E_v = E_v[\rho] \quad dE_v = \int \left( \frac{\delta E}{\delta \rho(r)} \right)_{v(\tau)} \delta \rho(r) d\tau
  $$

  with

  $$
  \mu = \left( \frac{\delta E}{\delta \rho(r)} \right)_{v(\tau)} \quad \text{(Euler equation)}
  $$

  $$
  dE_v = \mu \int \delta \rho(r) d\tau = \mu dN
  $$

  $\mu = \left( \frac{\partial E}{\partial N} \right)_{v(\tau)} = - \chi$ (Iczkowski - Margrave electronegativity)
From first order perturbation theory it can further be shown that

$$\rho(r) = \left( \frac{\delta E}{\delta v(r)} \right)_N$$

Identification of two first derivatives of $E$ with respect to $N$ and $v(r)$ in a DFT context.

$$\left( \frac{\partial^2 E}{\partial N^2} \right)_v = \eta \quad \text{Chemical Hardness} \quad S = \frac{1}{\eta} \quad \text{Chemical Softness}$$

$$\left[ \frac{\delta \mu}{\delta v(r)} \right]_N = \left( \frac{\partial \rho(r)}{\partial N} \right)_v = f(r) \quad \text{Fukui function} \quad S_f(r) = s(r) \quad \text{Local Softness}$$

2. Information carriers: from $\rho \rightarrow \sigma$

The shape function: an even simpler carrier of information?

**Introduction**


$$\sigma(r) = \frac{\rho(r)}{N}$$

shape function

- characterizes shape of the electron distribution
- redistributes $N$ in space $\rho(r) = N \sigma(r)$
  
  cf. Electronic Fukui Function: redistributes $S$ in space
  
  $$s(r) = Sf(r)$$

- $\int \sigma(r) d\Gamma = 1$

**$\sigma(r)$ as carrier of information**


- $\sigma(r) \rightarrow v(r)$ for a finite Coulombic system

Cfr. Bright Wilson’s arguments for the $\rho(r) \rightarrow v(r)$ relationship
Water:

Ethylene:

Integration $\rightarrow N$

Cusps $\rightarrow Z_A, R_A \rightarrow \nu(r)$

$\rho(r) \rightarrow N, \nu(r) \rightarrow H_{op} \rightarrow "Everything"$

- Cusps in $\rho$ and $\sigma$ occur at the same places as $\sigma(\mathbf{r}) = \frac{1}{N} \rho(\mathbf{r})$ (2)

- It is easily seen that

$$ Z_A = -\frac{1}{2} \left( \frac{1}{\sigma(\mathbf{r})} \frac{\partial \sigma(\mathbf{r})}{\partial \mathbf{r} \cdot \mathbf{r} - R_A} \right)_{\mathbf{r} = R_A} $$

$$ \sigma(\mathbf{r}) \rightarrow \{ R_A, Z_A \} \rightarrow v(\mathbf{r}) $$

- $\sigma(\mathbf{r}) \rightarrow N$ - Convexity postulate

- Long range behaviour of $\rho(\mathbf{r})$
What about $N$?

- Convexity postulate

$$E_1 - E_2 > E_2 - E_3 > E_3 - E_4 \ldots \text{ until system becomes unbound}$$

- Successive ground state ionisation potentials of a coulombic system increase

- Long range behaviour of $\rho(r)$

$$\rho(r) \xrightarrow{r \uparrow} e^{-\sqrt{8}r}$$

(For a simple approach: see N.C. Handy in European Summer School in Quantum Chemistry, Lund University, Chapter 10, 2000)
A first application: $\sigma(r)$ contains enough information to predict atomic Ionization Potentials.

Expressing the ionization energy in terms of moments of the shape function

$$
\mu^{(n)}_\kappa [\sigma] = \left( \int_0^\infty r^\kappa \sigma(r) 4\pi r^2 dr \right)^{n/\kappa}
$$

$$
IE[\sigma] = \sum_{\kappa=1}^N b_\kappa \mu^{(2)}_\kappa [\sigma]
$$

Neutral atoms and cations

$$
H \rightarrow W^{20^+}
$$

(1081 species)

Already only two moments of $\sigma$ give a fair fit with the data, whereas two moments of the density are not adequate at all ($\sigma$ better for periodic properties)

σ(\(r\)) as carrier of information on DFT reactivity indices

Does the shape function also contain information about reactivity indices \(\eta, S, f(r), s(r), \ldots\) containing \(N\) derivatives?

- The long range behaviour of the Fukui Function

\[
\rho(\mathbf{r}) = A(N)e^{-\sqrt{8}I r} \quad \text{large } r
\]

\[
f(\mathbf{r}) = \left( \frac{\partial \rho(\mathbf{r})}{\partial \mathbf{N}} \right) \xrightarrow{v} \lim_{r \to \infty} \frac{\partial}{\partial r} \ln f(\mathbf{r}) = -\sqrt{8}I r
\]

\[
r \to \infty: \quad \frac{f(r)}{\rho(r)} \to \frac{\partial}{\partial r} \left( \frac{f(r)}{\rho(r)} \right) = \left( \frac{-2}{\sqrt{2}I} \right) \left[ \frac{\partial I}{\partial \mathbf{N}} \right]_v
\]

\[
\left| \frac{\partial I}{\partial \mathbf{N}} \right|_v \to \eta
\]
Now
\[
\frac{\partial}{\partial r} \left( \frac{f(r)}{\rho(r)} \right) = \frac{\partial}{\partial r} \left( \frac{\partial \sigma / \partial N}{\sigma} \right) = -\frac{2}{\sqrt{21}} \left( \frac{\partial I}{\partial N} \right)_v
\]

Simultaneous knowledge of \( \sigma(r) \) and \( \partial \sigma(r) / \partial N \rightarrow \eta \)


Case Study I: An Application of the $\sigma(r)$ Information Content: Quantum Similarity of Atoms

Quantum Similarity: Basics

• Characterizing similarity of molecules A and B

$\downarrow$ Electron density $\rho(r)$ $\Rightarrow$ smallest value $\int |\rho_A - \rho_B|^2 dr$

$\Rightarrow$ largest value for $Z_{AB} = \int \rho_A(r)\rho_B(r) dr$

$\Rightarrow$ Normalized index

$$Z_{AB} = \frac{\int \rho_A(r)\rho_B(r) dr}{\left( \int \rho_A^2(r) dr \right) \left( \int \rho_B^2(r) dr \right)^{1/2}}$$

M. Carbo et al., Int. J. Quant., 17, 1185 (1980)

$$= \frac{\int \sigma_A(r)\sigma_B(r) dr}{\left( \int \sigma_A^2(r) dr \right) \left( \int \sigma_B^2(r) dr \right)^{1/2}}$$

$\sigma(r)$
The case of atoms

Carbo type Approach

\[ Z_{AB} = \int \rho_A(r) \rho_B(r) \, dr \]

\[ SI = \frac{Z_{AB}}{\sqrt{Z_{AA} Z_{BB}}} \]

Numerical Hartree Fock wave functions

Noble Gases

Nearest neighbours alike!
Looking for periodicity: the introduction of Information Theory

- **Kullback Leibler Information Deficiency** \( \Delta S \) for a continuous probability distribution

\[
\Delta S(p_k|p_0) \equiv \int p_k(x) \log \frac{p_k(x)}{p_0(x)}
\]


\( p_k(x), p_0(x) \): normalized probability distributions, \( p_0(x) \): prior distribution.

\( \Delta S = \) distance in information between \( p_k(x) \) and \( p_0(x) \) or as the information present in \( p(x) \), distinguishing it from \( p_0(x) \)

\[\rightarrow \text{Choice of reference} \quad p_0(x)\]
Take $\rho(r)$ as $p(x)$

$$\int \rho_A(r) \log \frac{\rho_A(r)}{\rho_0(r)} \, dr$$

Choice of $\rho_0(r)$ leads to

Cf. Sanderson electronegativity scale

$$\frac{N_A}{N_0} \rho_0(r)$$

Renormalized density of a hypothetical noble gas atom with equal number of electrons as atom A.
\[ \Delta S_{A^\rho} = \int \rho_A(r) \log \frac{\rho_A(r)}{\rho_0(r)} \, dr \]
Eliminating $N_A$ dependence by reformulation of the theory directly in terms of the shape functions (cf. role as information carrier)

$$\Delta S_A \sigma = \int \sigma_A (r) \log \frac{\sigma_A (r)}{\sigma_0 (r)} \, dr$$

Reference choice as before: the core of the atom i.e. the shape of the previous noble gas atom
\[ \Delta S_A \sigma = \int \sigma_A(r) \log \frac{\sigma_A(r)}{\sigma_0(r)} \, dr \]

Periodicity and evolution in atomic properties throughout PT regained

Similarity Measure based on a **local** version of Kullback’s Information Discrimination

- Consider \( \Delta S^\rho_A (r) = \rho_A (r) \log \frac{\rho_A (r)}{\rho_0 (r)} \frac{N_A}{N_0} \)

- \( Z_{AB} = \int \Delta S^\rho_A (r) \Delta S^\rho_B (r) \, dr \)

Quantum Similarity Measure (QSM) 
Quantum Similarity Index

- Cross Section of QSM\((Z_A, Z_B)\)

\[
SI = \frac{Z_{AB}}{\sqrt{Z_{AA} \sqrt{Z_{BB}}}}
\]

\( Z_B = 82 \)
Information contained in the shape function of Nitrogen to determine that of the elements of the next row

\[
\begin{array}{cccccc}
N & \text{Al} & \text{Si} & \text{P} & \text{S} & \text{Cl} \\
0.9865 & 0.9969 & 1.0 & 0.9973 & 0.9903 \\
\end{array}
\]

A different aspect of Periodicity Regained
Relativistic Effects

Dirac Fock densities

\[ \rho(r) = \frac{1}{4\pi} \sum_{n \kappa} \frac{P_{n\kappa}^2(r) + Q_{n\kappa}^2(r)}{r^2} q_{n\kappa}. \]

- large and small components
- \( q_{n\kappa} \): occupation number of relativistic subshell

Similarity Index between HF and DF densities

Case Study II: Information (Theory) in Molecules: Similarity of enantiomers and the Holographic Density Theorem

Introduction

Enantiomers $\iff$ Different chemical behaviour towards chiral partners (e.g. receptors)

$\downarrow$

Medicinal Chemistry, Pharmacology

$\downarrow$

Eudesmic Ratio (ER) = Potency ratio of eutomer and distomer

$\uparrow ?$

Relationship with • (dis)similarity of enantiomers $?$ (Richards)

• degree of chirality $\iff$ Black-white or discrete property

Testing the Holographic Density Theorem through Hirshfeld partitioning of $\rho(r)$
The Holographic Density Theorem

Hohenberg - Kohn

\[ E = E_v[\rho] \]

\( \rho(r) \) for a ground state

compatibility with a single external potential \( v(r) \)

\( \rho(\Omega)(r) \)


\[ E = E_v[\rho_\Omega] \]
Hirshfeld partitioning: basics and information theory context


  \[ \rho_A(r) = w_A(r) \rho(r) \]

  Contribution of atom A to electron density at position \( r \)

  weight factor \( \frac{\rho_A(r)}{\sum_{X} \rho_X^0(r)} \) promolecular densities → “stockholder” partitioning

- **Nalewajski - Parr** ([Proc. Natl. Acad. Sci. USA, 97, 8879 (2000)])

  \( P_0(r) \) reference, well-behaved, probability distribution

  \( P(r) \) trial probability distribution whose information content we want to make as close as possible to \( P_0 \), subject to one or more constraints

  Define

  \[ \Delta S[P/P_0] = \int P(r) \ln \left( \frac{P(r)}{P_0(r)} \right) dr \]

  \[ \rho_A(r) = \frac{\rho_A^0(r)}{\rho_0^0(r)} \rho(r) \]

  Hirshfeld’s “stockholder” partitioning

  → Possibility to look at global and local similarity
Results (Carbo index)

CHFCIBr: the text-book example of a chiral molecule

• orientational problem: superimposing C* and two of its substituents
  \[\rightarrow 6\] orientations
• intuitively: superposition of C*, Cl, Br \[\rightarrow\] largest similarity
  \[\rightarrow\] adequate for local similarity analysis

Global similarity: B3PW91/6-311G* Carbo Index

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<th>superimposed atoms</th>
<th>Analytical</th>
<th>Numerical</th>
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<tbody>
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<td>ClBr</td>
<td>0.990</td>
<td>0.990</td>
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<tr>
<td>FCBr</td>
<td>0.915</td>
<td>0.915</td>
</tr>
<tr>
<td>HCBr</td>
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</tr>
<tr>
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<td>0.098</td>
</tr>
<tr>
<td>HCCI</td>
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<td>0.089</td>
</tr>
<tr>
<td>HCF</td>
<td>0.054</td>
<td>0.055</td>
</tr>
</tbody>
</table>

• Numerical and analytical results quasi identical (10^-3)
• Effect of orientation
Relative orientation of the R and S enantiomers of CHFCIBr: the asymmetric carbon atoms, chlorine and bromine are superimposed.
Local similarity via Hirshfeld partitioning

Calculation on the basis of
- $\rho$ but importance of core electrons, e.g. $C_{1S}$
- $\Delta\rho$: deformation density: $\Delta\rho = \rho - \rho^0$ $\rho^0 =$ promolecular density

<table>
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<th>$\rho$</th>
<th>$\Delta\rho$</th>
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<td>1.000</td>
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<tr>
<td>HCBr</td>
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</tr>
<tr>
<td>HCCI</td>
<td>0.971</td>
<td>0.995</td>
</tr>
</tbody>
</table>

- For C: larger range with $\Delta\rho$
  $\Delta\rho$ gives complementary information (role of core electrons eliminated)
- For H: numerical evidence for Holographic Density Theorem.
  "Chirality is everywhere"
Conclusions

• As all $\rho$ and $\Delta \rho$ results are identical to $\sigma$ and $\Delta \sigma$ results $\Rightarrow$
  (Dis)similarity of enantiomers = a shape function analysis

• Transition from global to local (dis)similarity

• First ab initio numerical testing of the Holographic Electron Density Theorem


• Confirmed by studies on systems with two asymmetric centra
  (halogensubstituted ethanes)

• An excursion into the relation with optical rotation

The case of substituted allenes: systems without C*

Sequences correspond with the sequence of the size of the substituents

→ As the substituents get larger, the optical rotation increases and the enantiomers become more and more dissimilar

• An information theory based approach to (dis)similarity of Enantiomers

\[
\Delta S \left[ \frac{\sigma_R}{\sigma_S} \right] = \int \sigma_R (r) \ln \left( \frac{\sigma_R (r)}{\sigma_S (r)} \right) dr
\]

Information in R distinguishing it from S

Local

Local version for atom A

\[
\Delta S \left[ \frac{\sigma_{A,R}}{\sigma_{A,S}} \right] = \int w_{A,R} \sigma_R (r) \ln \left( \frac{w_{A,R} \sigma_R (r)}{w_{A,S} \sigma_S (r)} \right) dr
\]

\[
w_{A,R} = \frac{\rho_{A,R} (r)}{\sum_x \rho_{X,R} (r)}
\]

Return to CHFClBr
(including also I as substituent)

Local entropy of C*

---

Conclusions

• Shape function contains basic information to look at dissimilarity of enantiomers at both global and local level

• Various functionals from \( \rho \) and \( \sigma \) are conceivable to extract information from it: Carbo Index,... local entropy based expressions.

• Dissimilarity of enantiomers permits chirality to pass from a black or white property to a continuously varying property, the “grey” scale being not evidently linked to optical rotation or constitution
3. The Holographic Shape Theorem

Holographic Density Theorem:

\[ \rho_{\Omega}(r) \text{ determines } \rho(r) \xrightarrow{\text{HK}} \text{ all properties} \]

\[ E = E_v[\rho_{\Omega}] \]

- Local similarity can never be perfect
  cf. The Chemist's idea of a molecule built up from functional groups, transferable from one molecule to another

* \( \rightarrow \) if \( \rho_{\Omega} \) identical in two different molecules
  \[ \Rightarrow \rho \text{ identical } \rightarrow \text{molecules identical} \]

Exact transferability is impossible, but the search for local similarity remains important because the theorem does not quantify the degree of resemblance of two \( \rho_{\Omega}(r) \) functions still allowing considerable variations of \( \rho(r) \) outside \( \Omega \).
The shape function $\sigma(r)$

- determines $v(r)$, $N \to$ all information on the system.
- cf. experimental set up of X-ray diffraction
  - $\rho(r)$ plots $\leftarrow$ complex transformation of refraction data whose intensities are measured relative to each other
  $\Rightarrow$ X-ray diffraction experiments initially yield the shape function

$\Rightarrow$ direct search for minimalization of $\int |\sigma_A(r) - \sigma_B(r)|^2 dr$

in Similarity Analysis

$\Rightarrow$ direct obtention of $Z_{AB}$ expression

$$Z_{AB} = \frac{\int \sigma_A(r)\sigma_B(r)dr}{\left[ (\int \sigma_A^2(r)dr) \left( \int \sigma_B^2(r)dr \right) \right]^{1/2}}$$
Combination of Holographic Theorem and the fundamental importance of the Shape Function

Knowledge of the shape function in a finite but otherwise arbitrary subdomain of a Coulombic system determines all properties of the system.

\[ \rho(r) = \sigma_N(r)N \]
From Hohenberg Kohn to a holographic shape theorem

a) Hohenberg - Kohn

\[
E = E_v[\rho]
\]

\(\rho(\mathbf{r})\) for a ground state

compatibility with a single external potential \(v(\mathbf{r})\)

\(v(\mathbf{r}), N\)

b) Mezey : Holographic density theorem

\[
E = E_v[\rho_{\Omega}]
\]

\(\rho_{\Omega}(\mathbf{r})\)

\(\Omega\) (finite, arbitrary subdomain)

\(\rho(\mathbf{r})\)

\(v(\mathbf{r}), N\)
c) Ayers : shape function

\[ \sigma(\tau) \rightarrow E = E_v[\sigma] \]

\[ \sigma(\tau) \rightarrow v(\tau), N \]

\[ \sigma(\tau) \rightarrow \sigma_\Omega(\tau) \rightarrow E = E_v[\sigma_\Omega] \]

\[ \sigma_\Omega(\tau) \rightarrow \sigma(\tau) \rightarrow v(\tau), N \]

\[ \rightarrow E = E_v[\sigma_\Omega] \]

Conclusion : Similarity in shape is a fundamental issue to be looked at, both globally and locally

Case Study III: Information Theory in Reactions: Kullback Leibler Information Profiles

- Investigation of information profiles for processes involving geometrical and energetical changes along a coordinate: internal rotation, vibrations, chemical reactions

- Kullback Leibler information deficiency along $\xi$

$$\Delta S \left[ \sigma_\xi (r)/\sigma_0 (r) \right] = \int \sigma_\xi (r) \ln \left( \frac{\sigma_\xi (r)}{\sigma_0 (r)} \right) dr$$

Shape function for reference geometry

- Can energetic relationships be retrieved/complemented from an information theory based analysis of the density or shape function

Cfr. Chemical Reaction

$\xi = \text{IRC}$
An example: $S_{N2}$ reaction $\text{OH}^- + \text{CH}_3\text{F} \rightarrow \text{CH}_3\text{OH} + \text{F}^-$

- Reaction Profile

- Take TS as reference
- $\Delta S[\sigma_\xi(r)/\sigma_{TS}(r)] = \text{distance in information between shape function of TS (}\sigma_{TS}\text{) and system along the reacton path (}\sigma_\xi\text{)}$
- By convention: $\Delta S=0$ at $\xi=0$ (TS)

$\Delta S$ profile
Comparison between energetical data and shape function information measure

\[ \Delta E_{\text{forward}} = 7.85 \text{ kcal mol}^{-1} \quad \Delta S[\sigma_R, \sigma_{TS}] = 1.83 \]

\[ \Delta E_{\text{reverse}} = 44.60 \text{ kcal mol}^{-1} \quad \Delta S[\sigma_P, \sigma_{TS}] = 3.44 \]

TS contains more information about reactants than about products

Much lower reaction barrier for forward than for reverse reaction

Hammond’s postulate ("exothermic reaction: early TS; endothermic reaction: late TS")

retrieved in the information profile related to the shape function

Other examples (rotation, vibration, ...)

Conclusions

• The electron density function as a carrier of information is challenged by an even simpler function: the shape function. The latter contains enough information for describing chemical reactivity and permits an extension of the Holographic Density Theorem.

• Information theory based analysis of the shape function of atoms reveals the periodicity in Mendeleev’s table.

• Information theory based Hirshfeld partitioning of the electron density of molecules paves the way to discuss local similarity in molecules, and in particular dissimilarity of enantiomers and to numerical studies on the Holographic Density Theorem.

• Information theory based reading of the Shape function along a reaction coordinate yields a companion to the energy profile of a reaction.
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