Entropy and complexity measures of D-dimensional systems with some atomic and molecular applications

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PART I

Fisher information and uncertainty relations

PART II

Measures of complexity and applications

Uncertainty measures

Power moments

$$\langle r^k \rangle = \int r^k \rho(\mathbf{x}) d\mathbf{x};\ k = 0, 1, 2, \ldots;\ r \equiv |\mathbf{x}|$$

$$\Longrightarrow \text{Variance } V_{\mathbf{x}} = \langle r^2 \rangle - \langle r \rangle^2$$

Entropic moments

$$W_{\mathbf{x}}^{(q)} = \int [\rho(\mathbf{x})]^q \, d\mathbf{x};\ q \geq 0$$

$$\Longrightarrow \text{Rényi entropy } R_{\mathbf{x}}^{(q)} = \frac{1}{1-q} \ln \int [\rho(\mathbf{x})]^q \, d\mathbf{x}$$

Shannon entropy

$$S_{\mathbf{x}} = -\int \rho(\mathbf{x}) \log \rho(\mathbf{x}) d\mathbf{x}$$

Uncertainty measures

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Shannon entropy

$$S_{\mathbf{x}} = -\int \rho(\mathbf{x}) \log \rho(\mathbf{x}) d\mathbf{x}$$

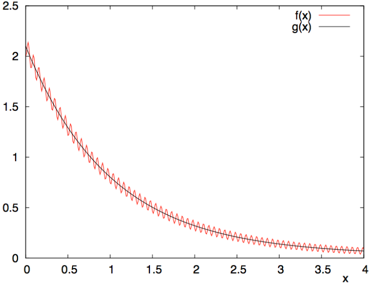
Fisher information

$$F_{\mathbf{x}} = \int \frac{|\nabla \rho(\mathbf{x})|^2}{\rho(\mathbf{x})} d\mathbf{x}$$

Mutual comparison

Let us take two simple densities

$$g(x) \sim e^{-ax}, \qquad f(x) \sim e^{-ax} + \epsilon \sin^2(nx)$$



It is found that

Function	Shannon entropy	Variance	Disequilibrium	Fisher information
$g(x)$	1.3485	0.07962	0.2690	9.3×10^{-1}
$f(x)$	1.3476	0.07966	0.2695	3.7×10^{3}

Fisher information

Fisher's information $F_{\mathbf{x}}$ is a very fertile concept! See e.g.:

B. Roy Frieden: Science from Fisher's information
Cambridge University Press, **2004**

Let us briefly mention:

- Basic variable of a variational methodology (E.P.I.) to obtain various fundamental equations of motion; e.g., Schrödinger, Dirac,. . .
- Indicator of the
  - periodicity and shell structure in the periodic table [MP 100 (**2002**) 3225],
  - avoided crossings of atoms and molecules in external fields [EPJD 32 (**2005**) 39],
  - stationary points and bond breaking/forming regions in chemical reactions [JCTC 6 (**2010**) 145].

Fisher information

- Closely related with various physical observables (kinetic and Weiszäcker energies,...).

- Measure of the position uncertainty of the particle.

  “The higher this quantity is, the more localized is the density, the smaller is the uncertainty and the higher is the accuracy in estimating the localization of the particle.”

Fisher information

Wavefunctions:

$$\psi(\mathbf{x}), \mathbf{x} \in \mathbb{R}^D; \qquad \tilde{\psi}(\mathbf{p}) = \frac{1}{(2\pi)^{\frac{D}{2}}} \int \psi(\mathbf{x}) e^{-i\mathbf{p}\mathbf{x}} d\mathbf{x}.$$

Associated probability densities

$$\rho(\mathbf{x}) = |\psi(\mathbf{x})|^2; \qquad \tilde{\rho}(\mathbf{p}) = |\tilde{\psi}(\mathbf{p})|^2.$$

Fisher informations:

$$F_{\mathbf{x}} = \int \frac{|\nabla_{\mathbf{x}} \rho(\mathbf{x})|^2}{\rho(\mathbf{x})} d\mathbf{x}; \qquad F_{\mathbf{p}} = \int \frac{|\nabla_{\mathbf{p}} \tilde{\rho}(\mathbf{p})|^2}{\tilde{\rho}(\mathbf{p})} d\mathbf{p}$$

Uncertainty relations

- Heisenberg-like relations.

$$\langle r^2\rangle\langle p^2\rangle \geq \frac{D^2}{4} \quad \text{[Z. Phys. 44 (\textbf{1927}) 326]}$$

$$\langle r^a\rangle^{\frac{2}{a}}\langle p^b\rangle^{\frac{2}{b}} \geq C(a,b,D) \quad \text{[PRA (\textbf{2011})]}$$

- Rényi-entropy-based relation [PRA 74 (**2006**) 052101; Phys. A 375 (**2007**) 499]

$$R_{\mathbf{x}}^{(q)} + R_{\mathbf{p}}^{(q)} \geq D \log\left[2\pi(2q)^{\frac{1}{2q-2}}(2q^*)^{\frac{1}{2q^*-2}}\right]; \quad \frac{1}{q}+\frac{1}{q^*}=2$$

- Shannon-entropy-based relation [CMP 44 (**1975**) 129]

$$S_{\mathbf{x}} + S_{\mathbf{p}} \geq D(1+\log\pi)$$

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- Shannon-entropy-based relation [CMP 44 (**1975**) 129]

$$S_{\mathbf{x}} + S_{\mathbf{p}} \geq D(1+\log\pi)$$

- Fisher-information-based relation [JPA 44 (**2011**) 065301]

$$F_{\mathbf{x}}F_{\mathbf{p}} \geq 4D^2$$

Aim

The relation

$$F_{\mathbf{x}}F_{\mathbf{p}} \geq 4D^2$$

provides a **new formulation of the position-momentum U.P.?**

Moreover, for arbitrary central potentials it is fulfilled that

$$F_{\mathbf{x}}F_{\mathbf{p}} \geq 16\left(1-\frac{2|m|}{2l+D-2}\right)\langle \mathbf{x}^2\rangle\langle \mathbf{p}^2\rangle$$

$$F_{\mathbf{x}}F_{\mathbf{p}} \geq 16\left(1-\frac{2|m|}{2l+D-2}\right)\left(l+\frac{D}{2}\right)^2$$

Fisher-information-based uncertainty relation

Theorem
If either $\psi(\mathbf{x})$ or $\tilde{\psi}(\mathbf{p})$ is real, then

$$F_{\mathbf{x}} F_{\mathbf{p}} \geq 4D^2$$

Proof
We want to minimize the product

$$G = F_{\mathbf{x}} F_{\mathbf{p}}$$

with the constraint

$$1 = \int |\psi(\mathbf{x})|^2 d\mathbf{x} \equiv \int u^2(\mathbf{x}) d\mathbf{x}; \quad u \equiv |\psi|.$$

Assuming $\tilde{\psi}(\mathbf{p}) = \tilde{\psi}^*(\mathbf{p})$, the momentum-space Fisher measure is

$$F_{\mathbf{p}} = \int \frac{|\nabla_{\mathbf{p}} \tilde{\rho}(\mathbf{p})|}{\tilde{\rho}(\mathbf{p})} d\mathbf{p} = 4 \int |\nabla_{\mathbf{p}} \tilde{\psi}(\mathbf{p})|^2 d\mathbf{p} = 4 \int \tilde{\psi}(\mathbf{p}) \nabla^2_{\mathbf{p}} \tilde{\psi}(\mathbf{p}) d\mathbf{p} = 4 \langle \mathbf{x}^2 \rangle.$$

Fisher-information-based uncertainty relation

So,

$$G = 4\langle \mathbf{x}^2 \rangle F_{\mathbf{x}} = 16 \left[\int u^2(\mathbf{x}) \mathbf{x}^2 d\mathbf{x} \right] \left\{ \int \left[\nabla_{\mathbf{x}} u(\mathbf{x}) \right]^2 d\mathbf{x} \right\}$$

Since this functional is invariant under the transformation

$$u(\mathbf{x}) \longrightarrow u_\lambda(\mathbf{x}) = \lambda^{\frac{D}{2}} u(\lambda \mathbf{x}),$$

the previous minimization is equivalent to the variational problem

$$\delta \left\{ 4 \int \left[\nabla_{\mathbf{x}} u(\mathbf{x}) \right]^2 d\mathbf{x} + \alpha \left[\int u^2(\mathbf{x}) d\mathbf{x} - 1 \right] + \beta \left[\int \mathbf{x}^2 u^2(\mathbf{x}) d\mathbf{x} - b \right] \right\} = 0$$

where α and β are the Lagrange multipliers.

Fisher-information-based uncertainty relation

It turns out that the associated Euler-Lagrange equations can be recast into the Schrödinger form

$$-\frac{1}{2}\nabla^2 u(\mathbf{x}) + V(\mathbf{x})u(\mathbf{x}) = -\frac{1}{8}\alpha u(\mathbf{x})$$

with the potential

$$V(\mathbf{x}) = \frac{1}{8}\beta \mathbf{x}^2$$

Then, the minimizer $u_m(\mathbf{x})$ corresponds to the ground state of $V(\mathbf{x})$; i.e.

$$u_m(\mathbf{x}) = \frac{1}{\left(\pi^{\frac{1}{2}} a\right)^{\frac{D}{2}}} e^{-\frac{\mathbf{x}^2}{2a^2}}, \quad \text{with } a = \left(\frac{4}{\beta}\right)^{\frac{1}{4}}.$$

Finally, the calculation of the position and momentum Fisher informations of this function gives

$$F_{\mathbf{x}} F_{\mathbf{p}} \geq 4D^2$$

■

The Fisher product $F_{\mathbf{x}}F_{\mathbf{p}}$ can be made arbitrarily small

Particular cases for $D = 1$, where $F_{\mathbf{x}}F_{\mathbf{p}} \ngeq 4$:

- Biparametric family of wfs.:

$$\psi(x) = \pi^{-\frac{1}{4}} e^{-\frac{x^2}{2}} \left[a_0 H_0(x) + \frac{a_1}{\sqrt{2}} H_1(x) \right]$$

where $H_n(x)$ is a Hermite polynomial of nth-order, and

$$a_0 = \epsilon_0 + i\sqrt{\frac{3}{4} - \epsilon_0^2}; \quad a_1 = \epsilon_1 + i\sqrt{\frac{1}{4} - \epsilon_1^2}$$

with real ϵ_0 and ϵ_1. Note that the w.f. is properly normalized, i.e.

$$|a_0|^2 + |a_1|^2 = 1, \quad \text{if } \epsilon_0 \leq \sqrt{\frac{3}{4}} \text{ and } \epsilon_1 \leq \frac{1}{2}.$$

Then, there are values of ϵ_0 and ϵ_1 such that $F_{\mathbf{x}}F_{\mathbf{p}} < 4$!, e.g.

$$\text{if } \left\{ \begin{array}{l} \epsilon_0 = 0.3 \\ \epsilon_1 = 0.4 \end{array} \right. \Longrightarrow \left\{ \begin{array}{l} F_{\mathbf{x}} \simeq 2.22 \\ F_{\mathbf{p}} \simeq 1.68 \end{array} \right. \Longrightarrow F_{\mathbf{x}}F_{\mathbf{p}} \simeq 3.73 < 4$$

The Fisher product $F_{\mathbf{x}}F_{\mathbf{p}}$ can be made arbitrarily small

- Multiparametric family of Hermite wavefunctions:

$$\psi_n(x) = \pi^{-\frac{1}{4}} e^{-\frac{x^2}{2}} \sum_{k=0}^{n} a_k \frac{1}{\sqrt{2^k k!}} H_k(x),$$

where a_k are complex coefficients such that $\sum_{k=0}^{n} |a_k|^2 = 1$. They span a linear subspace of the general space of normalized wavefunctions $\psi(x)$, $x \in \mathbf{R}$.

How many states, f_n, violate $F_{\mathbf{x}}F_{\mathbf{p}} \geq 4$?

To calculate f_n we use a numerical Monte Carlo approach:

a) Generate a large number A_n of random states $\psi_n(x)$ in the subspace, uniformly distributed according to the Haar measure. This is done by generating A_n n-tuples $(a_1, \dots, a_n)$.

b) Determine the number B_n of the A_n states which violate the inequality $F_{\mathbf{x}} F_{\mathbf{p}} \geq 4$.

c) Compute the ratio $f_n = \frac{B_n}{A_n}$ of states violating $F_{\mathbf{x}} F_{\mathbf{p}} \geq 4$.

Results:

n	f_n
2	0.33 ± 0.01
3	0.092 ± 0.009
4	0.030 ± 0.005
5	0.0093 ± 0.0009
6	0.0025 ± 0.0006

Remark:

As n increases, both A_n and B_n increases in such a way that its proportion f_n decreases very fast (as indicated in the previous table).

Conjecture:

The proportion f_n of states violating the uncertainty relation $F_{\mathbf{x}} F_{\mathbf{p}} \geq 4$ actually tends rapidly to zero when $n \rightarrow \infty$!!
i.e.,
there are actually plenty of complex wavefunctions satisfying the inequality $F_{\mathbf{x}} F_{\mathbf{p}} \geq 4$.
So, this U.R. might not be the most universal one.

Schrödinger equation for central potentials

The Schrödinger equation of D-dimensional particle in the central potential $V_D(r)$, $r \equiv |\mathbf{x}|$, is

$$\left[-\frac{1}{2}\nabla^2 + V_D(r)\right]\psi(\mathbf{x}) = E_D\psi(\mathbf{x})$$

In hyperspherical coordinates $\mathbf{x} = (r, \theta_1, \theta_2, \dots, \theta_{D-1}) \equiv (r, \Omega_{D-1})$, the wavefunctions are

$$\psi(\mathbf{x}) = R_{E,l}(r)\mathcal{Y}_{\{\mu\}}(\Omega_{D-1}),$$

where $\{\mu\} = (l \equiv \mu_1, \mu_2, \dots, \mu_{D-1} \equiv |m|)$ have the values

$$l = 0, 1, 2, \dots, \qquad l \geq \mu_2 \geq \cdots \geq |\mu_{D-1}|,$$

and $\mathcal{Y}_{\{\mu\}}(\Omega_{D-1})$ stand for the hyperspherical harmonics.

Fisher information

and the radial wavefunctions $R_{E,l}(r)$ satisfy

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}-\frac{D-1}{r}\frac{d}{dr}+\frac{l(l+D-2)}{2r^2}+V_D(r)\right]R_{E,l}(r)=E_D R_{E,l}(r)$$

Then, **two relevant results** have been found:

- Exact expressions for the Fisher informations [JMP 47 (**2006**) 103504]

$$F_{\mathbf{x}}=4\langle\mathbf{p}^2\rangle-2(2l+D-2)|m|\langle\mathbf{x}^{-2}\rangle$$

$$F_{\mathbf{p}}=4\langle\mathbf{x}^2\rangle-2(2l+D-2)|m|\langle\mathbf{p}^{-2}\rangle$$

- Radial-uncertainty-like inequalities [JPA 40 (**2007**) 1845]

$$\langle\mathbf{p}^2\rangle\geq\left(l+\frac{D-2}{2}\right)^2\langle\mathbf{x}^{-2}\rangle$$

$$\langle\mathbf{x}^2\rangle\geq\left(l+\frac{D-2}{2}\right)^2\langle\mathbf{p}^{-2}\rangle$$

Product of Fisher informations

The combination of these results yields

$$F_{\mathbf{x}} \geq 4\left(1 - \frac{|m|}{2l + D - 2}\right)\langle \mathbf{p}^2 \rangle$$

$$F_{\mathbf{p}} \geq 4\left(1 - \frac{|m|}{2l + D - 2}\right)\langle \mathbf{x}^2 \rangle$$

And then we have

$$F_{\mathbf{x}} F_{\mathbf{p}} \geq 16\left(1 - \frac{2|m|}{2l + D - 2}\right)^2 \langle \mathbf{x}^2 \rangle \langle \mathbf{p}^2 \rangle$$

which clearly manifests the uncertainty character of the Fisher product.

Uncertainty relation for central potentials

Using the general Heisenberg-Kennard relation

$$\langle \mathbf{x}^2 \rangle \langle \mathbf{p}^2 \rangle \geq \frac{D^2}{4}$$

one finds the U.R.

$$F_{\mathbf{x}} F_{\mathbf{p}} \geq 4D^2 \left(1 - \frac{2|m|}{2l + D - 2} \right)^2$$

Further improvement:

The use of the H-K relation for central potentials [NJP 8 (**2006**) 330]

$$\langle \mathbf{x}^2 \rangle \langle \mathbf{p}^2 \rangle \geq \left(l + \frac{D}{2} \right)^2$$

allows one to find [JPA 40 (**2007**) 1845]

$$F_{\mathbf{x}} F_{\mathbf{p}} \geq 16 \left(1 - \frac{2|m|}{2l + D - 2} \right)^2 \left(l + \frac{D}{2} \right)^2$$

Remark that for $l = m = 0$, one recovers the relation $F_{\mathbf{x}} F_{\mathbf{p}} \geq 4D^2$.

Fisher informations of hydrogenic systems

Potential $V(\mathbf{x}) = -\frac{Z}{r}$; $r \equiv |\mathbf{x}|$, $\mathbf{x} = (r, \theta_1, \ldots, \theta_{D-1})$.
Position-space probability density

$$\rho(\mathbf{x}) = N_{n,l}^2 \tilde{r}^{2l} e^{-\tilde{r}} \left[L_{n-l-1}^{(2l+D-2)}(\tilde{r}) \right]^2 \left| \mathcal{Y}_{\{\mu\}}(\Omega_{D-1}) \right|^2$$

with

$$\tilde{r} = \frac{2Z}{\eta} r \quad \text{and} \quad \{\mu\} = (l \equiv \mu_1, \mu_2, \ldots, \mu_{D-1}).$$

Momentum-space probability density

$$\rho(\mathbf{p}) = K_{n,l}^2 \frac{(\eta p)^{2l}}{(1+\eta^2 p^2)^{2l+D+1}} \left[C_{n-l-1}^{\left(l+\frac{D-1}{2}\right)} \left(\frac{1-\eta^2 p^2}{1+\eta^2 p^2} \right) \right]^2 \left| \mathcal{Y}_{\{\mu\}}(\Omega_{D-1}) \right|^2$$

with

$$\eta = n + \frac{D-3}{2}$$

Results

[JMP 47 (**2006**) 052104] and [IJQC 110 (**2010**) 1529]
The Fisher information has the values

$$F_{\mathbf{x}} = \frac{4Z^2}{\eta^3}(\eta - \mu_{D-1})$$

in position space, and

$$F_{\mathbf{p}} = \frac{2\eta^2}{Z^2}\left[5\eta^2 - 3L(L+1) - (8\eta - 6L - 3)\mu_{D-1} + 1\right]$$

in momentum space, with $L = l + \frac{D-3}{2}$.
Then, the Fisher uncertainty product is given by

$$F_{\mathbf{x}}F_{\mathbf{p}} = \frac{8(\eta - \mu_{D-1})}{\eta}\left[5\eta^2 - 3L(L+1) - (8\eta - 6L - 3)\mu_{D-1} + 1\right]$$

which does not depend on Z.

Results for $D = 3$ quantum systems

The Fisher information for three-dimensional systems are

$$F_{\mathbf{x}} = \frac{4Z^2}{\eta^3}(n - m)$$

$$F_{\mathbf{p}} = \frac{2n^2}{Z^2}\left[5n^2 - 3l(l+1) - (8n - 6l - 3)m + 1\right]$$

in position and momentum space, respectively.

So, the Fisher uncertainty product is

$$F_{\mathbf{x}}F_{\mathbf{p}} = \frac{8(n-m)}{n}\left[5n^2 - 3l(l+1) - (8n - 6l - 3)m + 1\right]$$

Conclusions

- A new formulation of the U.P. based on Fisher's information has been shown for real (either position or momentum) wavefunctions.
- The Fisher-information-based U.R. for arbitrary central potentials has been found.
- The Fisher uncertainty product for hydrogenic systems has been explicitly given.

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    - Uncertainty measures
    - Fisher information
    - Uncertainty relations
    - Central potentials
    - Hydrogenic systems
    - Conclusions and references

2. Measures of complexity and applications
    - Measures of complexity
    - Hydrogenic applications
    - Relativistic effects
    - Dimensionality effects
    - Molecular applications
    - Conclusions and references

Measures of complexity

Fisher-Shannon complexity

$$C_{\mathsf{FS}}[\rho] = F[\rho] \times \frac{1}{2\pi e} \exp\left(\frac{2}{3} S[\rho]\right)$$

LMC shape complexity

$$C_{\mathsf{LMC}}[\rho] = \langle \rho \rangle \times \exp\left(S[\rho]\right)$$

Cramér-Rao complexity

$$C_{\mathsf{CR}}[\rho] = F[\rho] \times V[\rho]$$

Hydrogenic information theory

[Intern. J. Quantum Chem. 110 1529, 2010] (e.g. hydrogen-like atoms and ions, exotic atoms, Rydberg atoms, antimatter atoms, qubits, . . .)

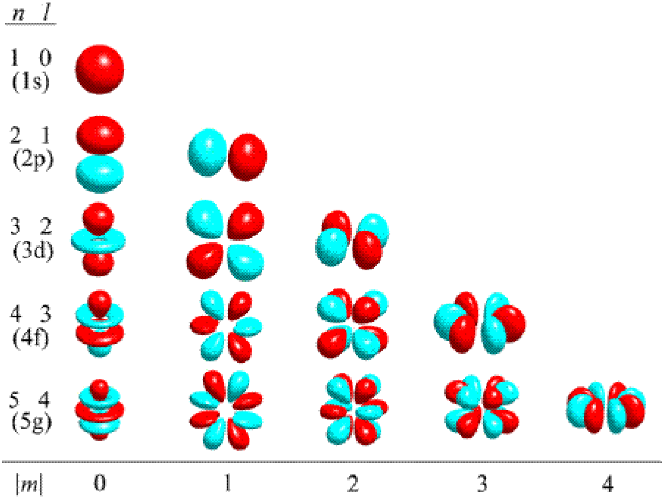
- Coulomb potential $V(\vec{r}) = -\frac{Z}{r}$
- Quantum states
  - Energies: $E_n = -\frac{Z^2}{2n^2}$
  - Probability density: $\rho_{nlm}(\vec{r}) = |\Psi_{nlm}(\vec{r})|^2 = R_{nl}^2(r)\,|Y_{lm}(\theta,\phi)|^2$ where

$$R_{nl}^2(r) = \frac{4Z^3}{n^4}\tilde{r}^{-1}\omega_{2l+1}(\tilde{r})\left[\tilde{L}_{n-l-1}^{(2l+1)}(\tilde{r})\right]^2$$

with

$$\tilde{r} = \frac{2Z}{n}r; \qquad \omega_\alpha(x) = x^\alpha e^{-x}$$

Quasicircular states $(n, l = n - 1)$



Hydrogenic information theory

Spreading measures

- The Heisenberg measure

$$V\left[\rho_{nlm}\right]=\frac{1}{4Z^3}\left[n^2(n^2+2)-l^2(l+1)^2\right]$$

with

- $n=1,2,...$
- $l=0,1,..,n-1.$

It doesn't depend on m

Hydrogenic information theory

[Eur. Phys. J. D. **55**,539,2009]

- The Fisher information

$$F\left[\rho_{nlm}\right]=4\left\{\int_0^\infty\left\{\frac{d}{dr}\left[\sqrt{\omega_{2l+1}}L_{n-l-1}^{(2l+1)}\right]\right\}^2 dr\right.$$
$$\left.+N_{n-l-1}\int_\Omega\left|\frac{d}{d\theta}Y_{lm}(\theta,0)\right|^2 d\Omega\right\}$$
$$=\frac{4Z^3}{n^3}(n-|m|)$$

with

- $n=1,2,...$
- $l=0,1,..,n-1.$
- $m=-l,-l+1,...,l$

It doesn't depend on l

Hydrogenic information theory

- The Shannon entropy

$$S[\rho_{nlm}] = S[R_{nl}] \times S[Y_{lm}]$$
$$= A(n,l,m) + \frac{1}{2n} E_1\left[L_{n-l-1}^{(2l+1)}\right] + E\left[C_{n-|m|}^{(|m|+\frac{1}{2})}\right] - 3\log Z$$

where the entropic integrals

$$E_i[p_k] := -\frac{1}{\pi}\int_a^b x^i p_k^2(x)\log\left[p_k^2(x)\right]\omega(x)dx; \quad i = 0,1$$

cannot be explicitly calculated except in the two cases:

Circular states $(n, l = m = n-1)$
Rydberg states (large and very large n)

In particular

$$S[\rho_{100}] = 3 + \log\pi - 3\log Z \qquad \text{for the Ground state}$$

and

$$S[\rho_{n00}] = 6\log n - \log 2 + 2\log\pi + o(1) \qquad \text{for (ns) Rydberg states}$$

Hydrogenic information theory

- LMC shape complexity

$$C_{\mathsf{LMC}}[\rho_{nlm}] := \langle \rho_{nlm} \rangle \times \exp\left(S[\rho_{nlm}]\right)$$

Since $\langle \rho_{nlm} \rangle = Z^3 D(n,l,m)$ one has

$$C_{\mathsf{LMC}}[\rho_{nlm}] = D(n,l,m) e^{B(n,l,m)}$$

where

$$B(n,l,m) = A(n,l,m) + \frac{1}{2n} E_1\left[L_{n-l-1}^{(2l+1)}\right] + E\left[C_{n-|m|}^{(|m|+\frac{1}{2})}\right]$$

and

$A(n,l,m)$ and $D(n,l,m)$ are explicitly known

Hydrogenic information theory

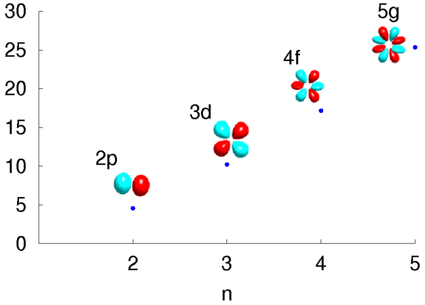
- Cramér-Rao complexity

$$\begin{aligned} C_{\mathsf{CR}}[\rho_{nlm}] &:= F[\rho_{nlm}] \times V[\rho_{nlm}] \\ &= \frac{n-|m|}{n^3}\left(n^2(n^2+2)-l^2(l+1)\right)^2 \end{aligned}$$

Hydrogenic information theory

- Fisher-Shannon complexity

$$C_{\mathsf{FS}}[\rho_{nlm}] := F[\rho_{nlm}] \times \frac{1}{2\pi e}\exp\left(\frac{2}{3}S[\rho_{nlm}]\right)$$
$$= \frac{4(n-|m|)}{n^3}\frac{1}{2\pi e}e^{\frac{2}{3}B(n,l,m)}$$



Hydrogenic information theory

Remarks

- The three complexity measures do not depend on Z!!!
- Dependence on the quantum numbers (n, l, m)
  - All increase with increasing n for (l, m) fixed.
  - All decrease with increasing l for (n, m) fixed.
  - All decrease with increasing m for (n, l) fixed.

Entropic and complexity measures of the ground state hydrogenic atom $(n=1, l=m=0)$

[Eur. Phys. J. D 55,539,2009]

- Entropic measures

  Shannon entropy

$$S[\rho_{100}] = 3 + \log \pi - 3 \log Z$$

  Fisher information

$$F[\rho_{100}] = 4Z^2$$

- Complexity measures

  Cramér-Rao

$$C_{\mathsf{CR}}[\rho_{100}] = 3$$

  LMC shape

$$C_{\mathsf{LMC}}[\rho_{100}] = \frac{e^3}{8}$$

  Fisher-Shannon

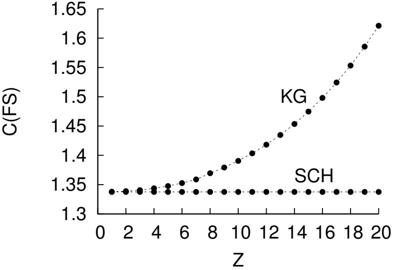
$$C_{\mathsf{FS}}[\rho_{100}] = \frac{2e}{\pi^{1/3}}$$

Fisher-Shannon complexity: relativistic indicator

[Europhys. Lett. **90**, 48001, 2010]

Pionic atom (pion mass = 273.13 au; nuclear charge = Z)

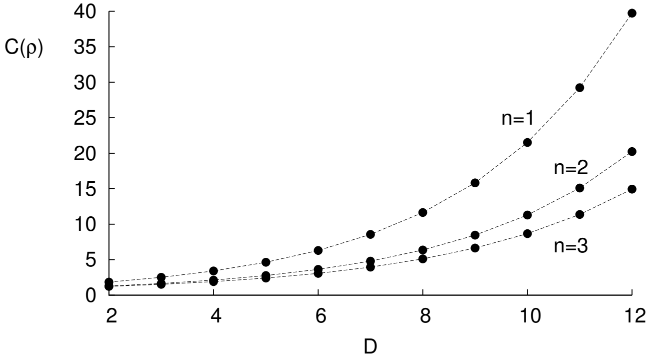
Schrödinger and Klein-Gordon treatments of the ground-state pionic atom yield the following dependence of the Fisher-Shannon complexity on Z:



LMC shape complexity: dimensionality indicator

[Physica A **388**, 3273, 2009; Int. J. Quant. Chem. **110**, 1529, 2010]

For circular states $(n, l = m = n - 1)$ of D-dimensional hydrogenic states, the LMC shape complexity has the form



Molecular complexity I

[PCCP **12**, 7108, 2010]

Goal: To quantify the information content of a set of 92 molecules with different geometries, composition and number of electrons N (isoelectronic groups with N between 10 and 49)

$$C(LMC) = \langle \rho \rangle \times e^{S}, \qquad C(FS) = F \times \frac{1}{2\pi e} e^{\frac{2}{3}S}$$

Chemical reactivity properties:

- Ionization potential (IP)
- Hardness: $\eta = \frac{1}{S} \sim \frac{\epsilon_{LUMO} - \epsilon_{HOMO}}{2}$.
- Electrophilicity: $\omega = \frac{\mu^2}{2\eta}$, with μ chemical potential.

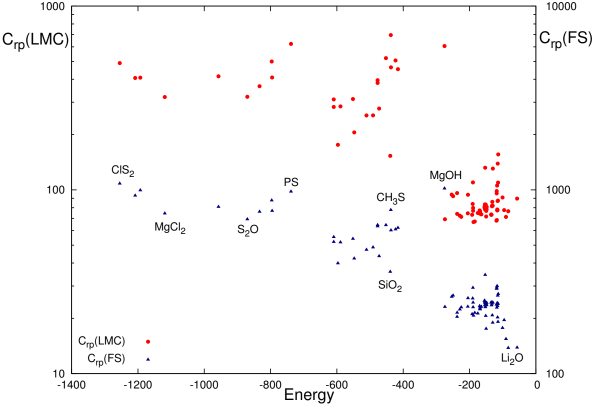
Note: we will present the results of complexity in phase space rp which is given by:

$$C_{rp} \equiv C_r \times C_p$$

for each complexity measure

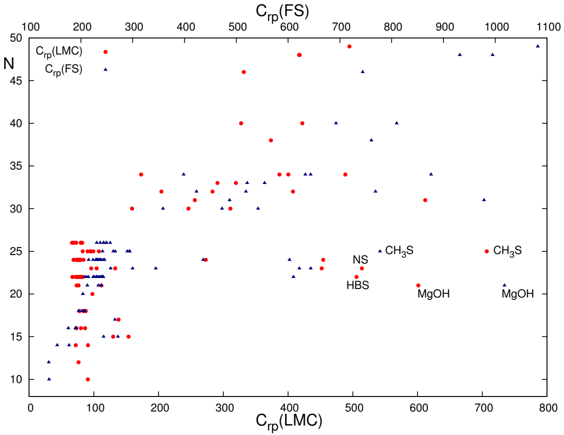
Molecular complexity II

Dependence on the molecular energy



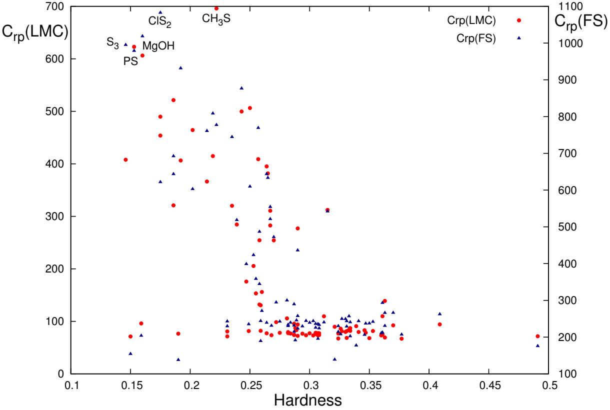
Molecular complexity III

Dependence on the number of electrons



Molecular complexity IV

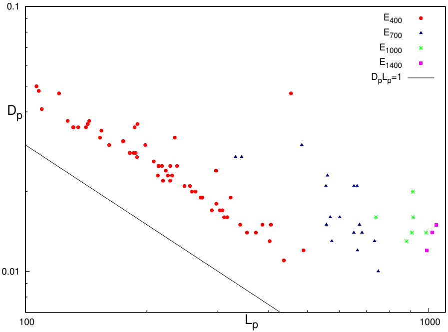
Dependence on hardness



Molecular complexity V

Information planes

- Disequilibrium-Shannon plane in momentum space for energetically different groups

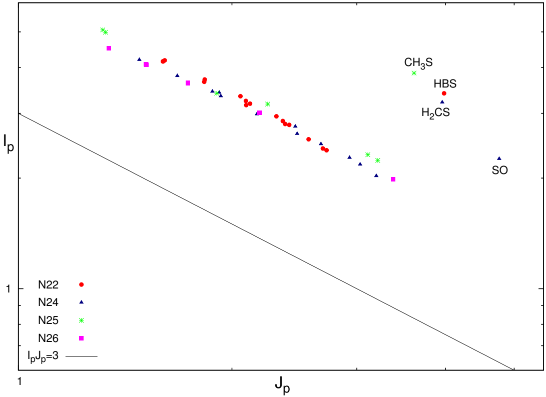


$$E_{400} \rightarrow E \geq -400$$
$$E_{700} \rightarrow E \in [-700, -400]$$
$$E_{1000} \rightarrow E \in [-1000, -700]$$
$$E_{1400} \rightarrow E \leq -1000$$

Molecular complexity VI

Information planes

- Fisher-Shannon plane in momentum space of isoelectronic series



Conclusions

Particular issues:

- The Shannon entropy predicts not only the atomic avoided crossings in presence of electromagnetic fields but also clearly shows the exchange of the information-theoretic character of the two states involved in this irregular spectral feature.
- The Fisher-Shannon complexity appears to be an indicator of the spatial geometry of the hydrogenic orbitals.
- The two-factor complexities are good quantitative estimators of the relativistic and dimensional effects of quantum systems.
- The molecular information planes in momentum space exhibit chemically significant patterns.

Conclusions

General:

- The information-theoretic concepts (e.g., entropies, two-component complexites and information planes) are useful tools to obtain a deeper insight into the internal disorder of atoms and molecules.

- The information-theoretic representation of the quantum systems complements the familiar energy-representation of the density-functional and wavefunction theories.

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